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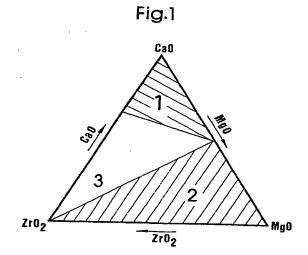
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#### Remarks:

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## (54) Saline soluble inorganic fibres

- (57) Use is disclosed, at temperatures of 1000°C or more for a period of 24 hours, of an inorganic fibre for which a vacuum cast preform of the fibre has a shrinkage of 3.5% or less when exposed to 1260°C for 24 hours and comprising CaO, SiO<sub>2</sub>, MgO, optionally ZrO<sub>2</sub>, optionally less than 0.75mol% Al<sub>2</sub>O<sub>3</sub>, any incidental impurities amounting to less than 2mol% in total, and in which
  - a) the  ${\rm SiO_2}$  excess (defined as the amount of  ${\rm SiO_2}$  calculated as remaining after the above named constituents are crystallised as silicates) exceeds 21.8mol%;
  - b) the amount of CaO is greater than the sum of the amount of MgO and twice the amount of ZrO<sub>2</sub>; and,
  - c) the calculated ratio of diopside to wollastonite does not lie in the range from more than that of fibre E32 to 5.25.



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#### Description

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This invention relates to saline soluble, non-metallic, amorphous, inorganic oxide, refractory fibrous materials. The invention particularly relates to glassy fibres having silica as their principal constituent.

Inorganic fibrous materials are well known and widely used for many purposes (e.g. as thermal or acoustic insulation in bulk, mat, or blanket form, as vacuum formed shapes, as vacuum formed boards and papers, and as ropes, yarns or textiles; as a reinforcing fibre for building materials: as a constituent of brake blocks for vehicles). In most of these applications the properties for which inorganic fibrous materials are used require resistance to heat, and often resistance to aggressive chemical environments.

Inorganic fibrous materials can be either glassy or crystalline. Asbestos is an inorganic fibrous material one form of which has been strongly implicated in respiratory disease.

It is still not clear what the causative mechanism is that relates some asbestos with disease but some researchers believe that the mechanism is mechanical and size related. Asbestos of a critical size can pierce cells in the body and so, through long and repeated cell injury, have a bad effect on health. Whether this mechanism is true or not regulatory agencies have indicated a desire to categorise any inorganic fibre product that has a respiratory fraction as hazardous, regardless of whether there is any evidence to support such categorisation. Unfortunately for many of the applications for which inorganic fibres are used, there are no realistic substitutes.

Accordingly there is a demand for inorganic fibres that will pose as little risk as possible (if any) and for which there are objective grounds to believe them safe.

A line of study has proposed that if inorganic fibres were made that were sufficiently soluble in physiological fluids that their residence time in the human body was short; then damage would not occur or at least be minimised. As the risk of asbestos linked disease appears to depend very much on the length of exposure this idea appears reasonable. Asbestos is extremely insoluble.

As intercellular fluid is saline in nature the importance of fibre solubility in saline solution has long been recognised. If fibres are soluble in physiological saline solution then, provided the dissolved components are not toxic, the fibres should be safer than fibres which are not so soluble. The shorter the time a fibre is resident in the body the less damage it can do. H. Förster in The behaviour of mineral fibres in physiological solutions (*Proceedings of 1982 WHO IARC Conference*, Copenhagen, Volume 2, pages 27-55(1988)) discussed the behaviour of commercially produced mineral fibres in physiological saline solutions. Fibres of widely varying solubility were discussed.

International Patent Application No. WO87/05007 disclosed that fibres comprising magnesia, silica, calcia and less than 10 wt% alumina are soluble in saline solution. The solubilities of the fibres disclosed were in terms of parts per million of silicon (extracted from the silica containing material of the fibre) present in a saline solution after 5 hours of exposure. The highest value revealed in the examples had a silicon level of 67 ppm. In contrast, and adjusted to the same regime of measurement, the highest level disclosed in the Förster paper was equivalent to approximately 1 ppm. Conversely if the highest value revealed in the International Patent Application was converted to the same measurement regime as the Förster paper it would have an extraction rate of 901.500 mg Si/kg fibre - i.e. some 69 times higher than any of the fibres Förster tested, and the fibres that had the highest extraction rate in the Förster test were glass fibres which had high alkali contents and so would have a low melting point. This is convincingly better performance even taking into account factors such as differences in test solutions and duration of experiment.

International Patent Application No. WO89/12032 disclosed additional fibres soluble in saline solution and discusses some of the constituents that may be present in such fibres. Among such constituents are ZrO<sub>2</sub> and this document claims (among other things) processes using fibres of composition (in weight %):- ZrO<sub>2</sub> 0.06-10%; SiO<sub>2</sub> 35-70%; MgO 0-50%; CaO 0-64.5%. However the patent actually discloses a much more limited range of zirconia containing materials and these are listed in Table 1 below ranked on silica content. None of the disclosed zirconia containing compositions were tested for shrinkage and hence usefulness in high temperature applications; all that these fibres were tested for was ability to withstand a fire test and Table 1 indicates that the results of this test were not very predictable; there does appear to be a trend with silica content but no trend is discernible with zirconia content.

European Patent Application No. 0399320 disclosed glass fibres having a high physiological solubility.

Further patent specifications disclosing selection of fibres for their saline solubility are European 0412878 and 0459897. French 2662687 and 2662688. PCT WO86/04807 and WO90/02713.

Table 1

Test	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	Fire test	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>
	wt%	wt%	wt%	wt%	wt%	Pass/Fail	mol%	mol%	mol%	mol%	mol%
174	63.5	35.55	0.33	0.88	0.21	Р	61.83	37.08	0.48	0.5	0.1

Continuation of the Table on the next page

Table 1 (continued)

Test	SiO <sub>2</sub> wt%	CaO wt%	MgO wt%	Al <sub>2</sub> O <sub>3</sub> wt%	ZrO <sub>2</sub> wt%	Fire test Pass/Fail	SiO <sub>2</sub> mol%	CaO mol%	MgO mol%	Al <sub>2</sub> O <sub>3</sub> mol%	ZrO <sub>2</sub> mol%
178	60	38.3	0.48	0.36	0.54	-	58.7	40.14	0.7	0.21	0.26
177	59.7	38.7	0.46	0.34	0.50	-	58.36	40.53	0.67	0.20	0.24
176	59.5	39.1	0.42	0.31	0.42	-	58.1	40.91	0.61	0.18	0.2
182a	59.4	34.9	2.06	0.38	2.31	Р	58.69	36.94	3.03	0.22	1.11
181	59.2	36.6	1.13	0.32	0.83	Р	58.8	38.94	1.67	0.19	0.4
179	59.2	37	0.98	0.35	0.58	Р	58.74	39.33	1.45	0.2	0.28
175	59.2	39.1	0.41	0.33	0.4	Р	57.99	41.03	0.6	0.19	0.19
183	59.05	34.84	3.08	0.3	2.65	• Р	57.65	36.44	4.48	0.17	1.26
186	59.05	36.94	2.57	0.38	3.27	Р	56.63	37.95	3.67	0.21	1.53
191	58.6	33.5	2.72	0.58	3.67	Р	58.21	35.65	4.03	0.34	1.78
192	58.4	33.2	2.59	0.65	3.69	Р	58.39	35.56	3.86	0.38	1.8
189	58.19	35.39	3.26	0.39	3.36	- -	56.59	36.87	4.73	0.22	1.59
184	57.96	35.17	3.55	0.42	3.11	F	56.44	36.69	5.15	0.24	1.48
190	57.86	35.66	3.22	0.36	3.37	.F	56.33	37.19	4.67	0.21	1.6
185	57.8	34.4	3.74	0.56	3.12	F	56.62	36.1	5.46	0.32	1.49
188	57.7	36	3	0.2	3.3	Р	56.31	37.64	4.36	0.12	1.57
187	56.88	36.45	4	0.32	3.3	-	54.86	37.66	5.75	0.18	1.55
193	56.65	31.9	3.35	3.35	4.5	F	56.66	34.18	4.99	1.97	2.19
180	54.3	32.75	10.2	1.29	0.58	F	51.41	33.22	14.39	0.72	0.27
182	46.85	29.2	20.6	2.03	0.84	F	42.42	28.33	27.8	1.08	0.37

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The refractoriness of the fibres disclosed in these various prior art documents varies considerably. The maximum service temperature of any of the above mentioned fibres (when used as refractory insulation) is up to 815°C (1500°F).

Among saline soluble commercial fibres usable at temperatures higher than 815°C are SUPERWOOL™ a fibre manufactured by The Morgan Crucible Company plc and which has a maximum use temperature of 1050°C and a composition of SiO<sub>2</sub> 65wt%; CaO 29wt%; MgO 5wt%; Al<sub>2</sub>O<sub>3</sub> 1wt%. A similar fibre is INSULFRAX™ a fibre made by Carborundum Company which has a continuous use limit of 1000°C (1832°F) and which melts at 1260°C (2300°F). This has a composition of SiO<sub>2</sub> 65w%; CaO 31.1wt%; MgO 3.2wt%; Al<sub>2</sub>O<sub>3</sub> 0,3wt% and Fe<sub>2</sub>O<sub>3</sub> 0.3wt%.

Use of ZrO<sub>2</sub> as a constituent in aluminosilicate fibres to provide high temperature resistance is known (see European 0144349). However it is by no means apparent that this effect is transferable to saline soluble fibres and the disclosure of International Patent Application No. WO89/12032 discussed above would tend to suggest that it is not.

The applicant's earlier International Patent Application WO93/15028 (from which this application claims priority) disclosed saline soluble fibres usable at temperatures in excess of 1000°C but gave no indication that fibres could be used at still higher temperatures. The applicants have found that some of the fibres disclosed in WO93/15028 (e.g. fibre A2-13 from Table 9 of WO93/15028) are in fact usable at temperatures of up to 1260°C and even higher. In general the applicants have found that fibres of specified compositions (including zirconia containing fibres) are usable at temperatures up to and beyond 1260°C. The applicants have realised that failure of fibres at high temperature occurs primarily upon devitrification of the fibre; if on devitrification insufficient silica is left the fibres will fail through having a shrinkage of greater than 3.5%. Accordingly the applicants have looked to what materials are formed on devitrification.

In the following where reference is made to a saline soluble fibre this is to be taken as meaning a fibre having a total solubility of greater than 10ppm in saline solution as measured by the method described below, and preferably having much higher solubility.

Figure 1 shows a three axis composition diagram for the constituents CaO, MgO, and ZrO<sub>2</sub>; this diagram omits all other constituents so that the sum of CaO, MgO, and ZrO<sub>2</sub> at all points is 100%. Silica is in excess at all points as described below.

For fibres where CaO > MgO + 2ZrO $_2$  all of the MgO is bound as CaO.MgO.2SiO $_2$ ; all of the ZrO $_2$  is bound as 2CaO.ZrO $_2$ .4SiO $_2$ ; and any excess CaO is bound as CaSiO $_3$ . These fibres lie in region 1 of Figure 1 and in the following are referred to as excess CaO fibres.

For fibres where MgO > CaO all of the CaO is bound as CaO.MgO.2SiO<sub>2</sub>; all of the ZrO<sub>2</sub> is bound as ZrO<sub>2</sub>.SiO<sub>2</sub>; and the excess MgO is bound as MgO.SiO<sub>2</sub>. These fibres lie in region 2 of Figure 1 and in the following are referred to as excess MgO fibres.

For the fibres in region 3 of Figure 1 where CaO > MgO and CaO < MgO -  $2ZrO_2$ , all of the MgO is bound as CaO. MgO. $2SiO_2$ , the rest of the CaO is bound as  $2CaO.ZrO_2.4SiO_2$ , and the excess  $ZrO_2$  is bound as  $ZrO_2.SiO_2$ . These fibres are referred to in the following as excess  $ZrO_2$  fibres.

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The applicants have defined a term "SiO<sub>2</sub> excess" which indicates the amount of silica left once the above mentioned constituents (CaO, MgO, and ZrO<sub>2</sub>) have crystallised. The value of SiO<sub>2</sub> excess is calculated by subtracting from the total quantity of silica present that amount that should crystallise as silicates with the other constituents CaO, MgO, and ZrO<sub>2</sub> assuming all of the CaO, MgO, and ZrO<sub>2</sub> crystallise as the materials mentioned above. In most of the compositions studied alumina is present to some extent and so the applicants also assume that alumina crystallises as Al<sub>2</sub>O<sub>3</sub>. SiO<sub>2</sub> and to calculate SiO<sub>2</sub> excess this quantity is subtracted also. Only the above named constituents are used in calculating the SiO<sub>2</sub> excess as other chemical constituents are present in only small amounts. For other chemical constituents similar considerations apply. It has been found by the applicants that when the SiO<sub>2</sub> excess is greater than 21.8mol% the fibres tend to have a resistance to temperature of up to 1260°C

The applicants have found that for the excess CaO compositions the situation is complicated by a eutectic formed between the two crystalline materials diopside (CaO.MgO.2SiO2) and wollastonite (CaSiO<sub>3</sub>) that has a damaging effect on high temperature resistance. Thus the present invention excludes those excess CaO compositions that have a calculated diopside to wollastonite ratio in the range 1.8 to 5.25.

The physical basis for the importance of SiO<sub>2</sub> excess may be that it indicates how much silica is left to maintain a glassy phase on crystallisation of the other constituents as silicate materials. Further, the silicate materials that form on devitrification may become liquid or flow at 1260°C so causing shrinkage.

The quantity of potentially fluxing constituents such as alkali metals and other incidental impurities (e.g., iron oxides) should be kept low.

Accordingly the present invention provides a refractory fibre for which a vacuum cast preform of the fibre has a shrinkage of 3.5% or less when exposed to  $1260^{\circ}$ C for 24 hours and comprising CaO,SiO<sub>2</sub>, MgO, optionally ZrO<sub>2</sub> and/or less than 0.75mol% Al<sub>2</sub>O<sub>3</sub>, any incidental unpurities amounting to less than 2mol% in total, and in which the SiO<sub>2</sub> excess (defined as the amount of SiO<sub>2</sub> calculated as remaining after the above named constituents are crystallised as silicates) exceeds 21.8mol%, with the proviso that, if the amount of CaO is greater than the sum of the amount of MgO and twice the amount of ZrO<sub>2</sub> the calculated ratio of diopside to wollastonite does not lie in the range 1.8 to 5.25.

The applicants have also found that for those fibres that have a satisfactory shrinkage at  $1260^{\circ}$ C the saline solubility of the fibres produced appears to increase with increasing amount of MgO present—whereas  $ZrO_2$  and  $Al_2O_3$  are detrimental to solubility. The invention therefore also provides preferred saline soluble fibres of the composition specified above and in which the MgO excess [defined as MgO -  $(ZrO_2 + Al_2O_3)$ ] is greater than 10mol%, such fibres tending to have a total solubility of MgO + SiO<sub>2</sub> - CaO of greater than 50ppm (see below for measurement details). More preferably the MgO excess is greater than 11.2mol% such fibres tending to have extremely high solubility of about 100ppm or more. Yet more advantageously, so far as solubility is concerned, the MgO excess is neater than 15.25mol%; all of the fibres measured having an MgO excess greater than 15.25mol% had solubilities in excess of 100ppm.

As a consequence of inventing these fibres the invention also provides a saline soluble fibre characterised in that a vacuum cast preform of the fibre has a shrinkage of 3.5% or less when exposed to 1260°C for 24 hours.

The applicants have investigated, for then saline solubility and refractoriness, a range of compositions based on CaO/MgO/SiO<sub>2</sub> fibres with additional constituents Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>. These fibres were formed by blowing the molten constituents from a melt stream in a conventional manner but the invention is not limited to blown fibres and also encompasses fibres formed by spinning or any other means.

Tables 2 & 3 show the results of these tests. Table 2 indicates for each the linear shrinkages at 800, 1000, 1200, and 1260°C (not all samples measured at every temperature); weight percent composition; mole percent composition (based on the constituents CaO, MgO, SiO<sub>2</sub> Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>); SiO<sub>2</sub> excess (as defined above) and, for the CaO excess fibres, the calculated diopside to wollastonite ratio. Table 3 indicates for each the weight percent composition; mole percent composition (based on the constituents CaO, MgO, SiO<sub>2</sub> Al2O<sub>3</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>); solubilities of various constituents; and MgO excess (as defined above). Each sample that has a satisfactory shrinkage of 3.5% or less at 1260°C is indicated by a composition shown in bold. Those compositions that fail to meet the shrinkage criterion are indicated in italics. Other compositions are shown falling within the described ranges but for which the high temperature shrinkage was not measured; these compositions are indicated in plain text. Those compositions where a fibre could not be made or where the fibre was of too poor a quality for the solubility to be measured are indicated with X's.

A pattern emerges which is described below with reference to Table 2.

The fibres above and including line A all have a  $SiO_2$  excess of less than 21.8mol% and all (where measured) fail the shrinkage criterion that a vacuum cast preform of the fibre has a shrinkage of less than 3.5% when exposed to 1260°C for 24 hours.

The fibres above and including line B and below line A all have a  $TiO_2$  content of greater than 1.25mol% and all fail the shrinkage criterion.

The fibres above and including line C and below line B all have a Al<sub>2</sub>O<sub>3</sub> content of greater than 0.75mol% and all fail the shrinkage criterion.

The fibres below line C are grouped according to their relative amounts of CaO.MgO, and ZrO<sub>2</sub> (i.e. as to their positions in Figure 1)

The fibres above and including line D and below line C are the excess MgO fibres (region 2 of Figure 1) and are sorted on SiO<sub>2</sub> excess.

The fibres above and including line E and below line D are the excess  $ZrO_2$  fibres (region 3 of Figure 1) and are sorted on  $SiO_2$  excess.

The fibres below line E are the excess CaO fibres and are sorted on the diopside to wollastonite ratio.

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The fibres above and including line F and below line E are excess CaO fibre for which the diopside to wollastonite ratio is greater than 5.25.

The fibres above and including line G and below line F are excess CaO fibre for which the diopside to wollastonite ratio is less than 5.25 but greater than 1.8.

The fibres below line G are excess CaO fibre for which the diopside to wollastonite ratio is less than 1.8.

Looking first to the excess MgO fibres most pass the shrinkage criterion at 1260°C (where tested). B7D, BZ-440C, 37C, and BZ-4150C all contain relatively high levels of  $Fe_2O_3$  (1.1wt% for B7D and 0.6wt% for the others).

D3 and D8 contain relatively high levels (0.71mol% and 0.74 mol%) of TiO<sub>2</sub> and it may be that this, in combination with other impurities, has led to failure. It should be noted that D9 has 0.65mol% TiO<sub>2</sub> and has a satisfactory shrinkage.

BZ-440A, B7A, BZ-4150A, and BZ-560B have warying amounts of Na<sub>2</sub>O present (0.3-1.0wt%) and this may contribute to their failure.

BZ-4150B has a  $Al_2O_3$  content of 0.64mol% and fails the shrinkage criterion. This should be contrasted with BZ-4150 which has a similar composition but with only 0.06mol%  $Al_2O_3$  and which passes the shrinkage criterion. In further contract BZ-560E has an alumina content of 0.62mol% and passes the shrinkage criterion; this composition has a much higher  $ZrO_2$  content than BZ-4150B and the applicant believe that the presence of  $ZrO_2$  allows the fibres to tolerate much higher levels of impurities than would otherwise be the case.

D3 only just fails with a shrinkage of 3.8% and B19 only has a shrinkage of 3.6% at 1260°C and both may in fact be errors in measurement.

Looking next to the excess ZrO<sub>2</sub> fibres all apart from BZ-407, BZ-429 and BZ-430 pass the shrinkage criteria at 1260°C (where tested). These results may indicate that the incidental impurities (shown as "Others" in Table 2) are having an effect as BZ-429 and BZ-430 show high levels of impurities (1.1 and 0.9 wt% respectively) that on analysis included 0.4 and 0.3 wt% respectively of Na<sub>2</sub>O. BZ-430 only just failed the shrinkage criterion (3.7% shrinkage) and this may be due to error in measurement.

Turning now to the excess CaO fibres the pattern is clear but not exact. Fibres that have a diopside to wollastonite ratio of between 5.25 and 1.8 fail the shrinkage criterion. Those with a diopside to wollastonite ratio outside this range tend to pass. The fit is not exact and the fibres that fail to meet the shrinkage criterion are the following.

Among the excess CaO fibres with a diopside to wollastonite ratio in excess of 5.25 those that fail the shrinkage criterion include BZ-418, and BZ-29 which have low enough shrinkages that they may be the result of experimental error and these fibres may in fact have a satisfactory shrinkage.

BZ-421, B13, BZ-422, BZ-417, and BZ-416 also fail and although initial indicators were that this had something to do with the level of CaO this now appears to be incorrect. The failure to meet the shrinkage criterion may be due to the presence of fluxing constituents or otherwise. A possible reason for failure of BZ-29 and BZ-421 may be their high Al<sub>2</sub>O<sub>3</sub> content (0.55 and 0.51 mol% respectively) acting alone or in combination with impurities.

For the excess CaO fibres having a diopside to wollastonite ratio of less than 1.8 the only fibre proven to fail was fibre E24 which although passing a 1260°C test failed a 1200°C test. This result may have been due to experimental error, fluxing components, or otherwise.

Table 3 shows the solubilities of the fibres shown in Table 2 but ranked on MgO excess. Although by no means exact it can be seen that there is a trend in total solubility that closely follows MgO excess.

In any event the trend appears to be that excess CaO fibres perform poorly (perhaps due to the formation of CaSiO<sub>3</sub> which is not formed in excess MgO or excess ZrO<sub>2</sub> fibres) whereas excess MgO and excess ZrO<sub>2</sub> fibres perform better. Taken to the extreme this would indicate that a high MgO, low CaO, low ZrO<sub>2</sub>, low Al<sub>2</sub>O<sub>3</sub> fibre would have very high solubility and low shrinkage. However the applicant's experience is that such fibres are difficult to form (see Compositions A2-33, (A2-32,A2-28). Equally fibres that are too high in SiO<sub>2</sub> are difficult or impossible to form. The exact boundaries are difficult to ascertain and this invention only encompasses fibres that meet the above stated shrinkage

requirements.

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The applicants have tested some fibres to higher temperatures.

Fibres BZ-400, BZ-440, BZ-48, and BZ-54 were tested to 1350°C and all failed having shrinkages in excess of 20%. Fibres BZ-400, BZ-36, BZ-46, and BZ-61 were tested to 1300°C and had shrinkages, respectively, of 6.2%, 17.9%, 19.6%, and 3.1%. BZ-61 is in the excess MgO region and the applicants surmise (since 2CaO.ZrO<sub>2</sub>.4SiO<sub>2</sub> is not formed in this region) that it is this constituent that causes failure at 1300°C.

The fact that fibre shrinkage is so dependent on temperature (the fibres failing over such short temperature ranges as 1260°C to 1300°C and 1300°C to 1350°C) is a clue as to how experimental errors may arise. In a typical experimental furnace running at a nominal 1260°C temperatures can easily range from 1250°C to 1270°C both physically (from front to back or centre to wall of furnace) and in time (as the furnace controller supplies or stops current to the furnace). A 20°C temperature difference could easily move a sample from a temperature at which it passes to one at which it fails the 3.5% shrinkage criterion. As mentioned above this may explain the shrinkages of just over 3.5% found for compositions B19, D3, BZ-430, BZ-418 and BZ-29.

During the shrinkage tests some of the sample preforms used were also inspected to ascertain whether they reacted adversely with the ceramic boards (alumina or mullite boards) on which they rested during the test. It was found that the excess CaO fibres with a diopside to wollastonite ratio of less than 1.8 reacted particularly badly with mullite boards and further that due to acicular crystal growth the fibres tended to lose strength.

The following describes in detail the methods used to measure shrinkage and solubility.

Shrinkage was measured by proposed ISO standard ISO/TC33/SC2/N220 equivalent to British Standard BS 1920, part 6,1986) with some modifications to account for small sample size. The method in summary comprises the manufacture of vacuum cast preforms, using 75g of fibre in 500cm³ of 0.2% starch solution, into a 120 x 65mm tool. Platinum pins (approximately 0.1-0.3mm diameter) were placed 100 x 45mm apart in the 4 corners. The longest lengths (L1 & L2) and the diagonals (L3 & L4) were measured to an accuracy of ±5µm using a travelling microscope. The samples were placed in a furnace and ramped to a temperature 50°C below the test temperature at 400°C/hour and ramped at 120°C/hour for the last 50°C to test temperature and left for 24 hours. The shrinkage values are given as an average of the 4 measurements.

It should be noted that although this is a standard way of measuring shrinkage of fibre it has an inherent variability in that the finished density of the preform may vary depending on casting conditions. Further it should be noted that fibre blanket will usually have a higher shrinkage than a preform made of the same fibre. Accordingly the 3.5% figure mentioned in this specification is likely to translate as a higher shrinkage in finished blanket.

The applicants have looked to the various incidental impurities that can occur in inorganic oxide refractory fibres (e.g. alkali oxides and iron oxide) and have found that the impurity levels that can be tolerated vary according to the proportions of the main constituents of the fibre. Fibres containing high levels of  $ZrO_2$  for example can tolerate higher levels of  $Na_2O$  or  $Fe_2O_3$  than fibres with low levels of  $ZrO_2$ . Accordingly the applicants propose a maximum level of incidental impurities of 2mol%, the maximum level that will be tolerable will however vary as mentioned above.

Solubility was measured by the following method.

The fibre was first chopped - 2.5 g of fibre (deshotted by hand) was liquidised with 250 cm³ of distilled water in a domestic Moulinex (Trade Mark) food blender for 20 seconds. The suspension was then transferred to a 500 cm³ plastic beaker and allowed to settle after which as much liquid as possible was decanted and the remaining liquid removed by drying in an oven at 110°C.

The solubility test apparatus comprised a shaking incubator water bath, and the test solution had the following composition:-

Compound	Name	Grains
NaCl	Sodium chloride	6.780
NH₄CI	Ammonium chloride	0.540
NaHCO <sub>3</sub>	Sodium bicarbonate	2.270
Na <sub>2</sub> HPO <sub>4</sub> .H <sub>2</sub> O	Disodium hydrogen phosphate	0.170
Na <sub>2</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> .2H <sub>2</sub> O	Sodium citrate dihydrate	0.060
H <sub>2</sub> NCH <sub>2</sub> CO <sub>2</sub> H	Glycine	0.450
H <sub>2</sub> SO <sub>4</sub> s.g. 1.84	Sulphuric acid	0.050

The above materials were diluted to 1 litre with distilled water to form a physiological-like saline solution.

0.500 grams  $\pm\,0.0003$  grams of chopped fibre was weighed into a plastic centrifuge tube and 25 cm<sup>3</sup> of the above saline solution added. The fibre and saline solution was shaken well and inserted into the shaking incubator water bath maintained at body temperature (37°C  $\pm\,$  1°C). The shaker speed was set at 20 cycles/minute.

After the desired period (usually 5 hours or 24 hours) the centrifuge tube was removed and centrifuged at 4500 revs/minute for approximately 5 minutes. Supernatant liquid was then drawn off using a syringe and hypodermic needle. The needle was then removed from the syringe, air expelled from the syringe, and the liquid passed through a filter (0.45 micron cellulose nitrate membrane filter paper [WCN type from Whatman Labsales Limited]) into a clean plastic bottle. The liquid was then analysed by atomic absorption using a Thermo Jarrell Ash Smith - Hiefje II machine.

The operating conditions were as follows using a nitrous oxide and acetylene flame:-

	ELEMENT	WAVELENGTH (nm)	BRAND WIDTH	CURRENT (mA)	FLAME
	Al	309.3	1.0	8	Fuel Rich
	SiO <sub>2</sub>	251.6	0.3	12	Fuel Rich
1	CaO	422.7	1.0	7	Fuel Lean
	MgO	285.2	1.0	3	Fuel Lean

The procedure and standards adopted for determining the above elements were as set out below.

SiO<sub>2</sub> can be determined without dilution up to 250 ppm concentration (1 ppm 1mg/Litre). Above this concentration an appropriate dilution was made volumetrically. A 0.1% KCl solution (0.1g in 100 cm<sup>3</sup>) was added to the final dilution to prevent ionic interference. NB If glass apparatus is used, prompt analysis is necessary.

From a stock solution of 1000 ppm pure ignited silica (99.999%)(fused with  $Na_2CO_3$  at 1200°C for 20 minutes in a platinum crucible (0.2500g  $SiO_2/2g$   $Na_2CO_3$ ) and dissolved in dilute hydrochloric acid (4 molar) made up to 250cm<sup>3</sup> with distilled water in a plastic volumetric flask) the following standards were produced:-

STANDARD (ppm SiO <sub>2</sub> )	STOCK SOLUTION (cm <sup>3</sup> )
10.0	1.0
20.0	2.0
30.0	3.0
50.0	5.0
100.0	10.0
250.0	25.0

Add 0.1% KCI to each standard before making to 100cm<sup>3</sup>.

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Aluminium may be measured directly from the sample without dilution. Standards of 1.0, 5.0 and 10.0 ppm AI may be used. For calibration readings are multiplied by 1.8895 to convert from AI to  $Al_2O_3$ .

A standard AI atomic absorption solution (e.g, BDH 1000 ppm AI) was bought and diluted using an accurate pipette to the desired concentration. 0,1% KCI was added to prevent ionic interference.

Calcium may require dilutions on the sample before determination can be carried out (i,e. x 10 and x 20 dilutions). Dilutions must contain 0.1% KCl.

A standard Ca atomic absorption solution (e.g. BDH 1000 ppm Ca) was diluted with distilled water and an accurate pipette to give standards of 0.5, 4.0 and 10.0 ppm. 0.1% KCl is added to prevent ionic interference. To convert readings obtained from Ca to CaO a factor of 1.4 was used.

Magnesium may require dilutions on the sample before determinations can be made (i.e. x 10 and x 20). Add 0,1% KCI to each dilution. To convert Mg to MgO multiply by 1.658.

A standard Mg atomic absorption solution (e.g. BDH 1000 ppm Mg) was diluted with distilled water and an accurate pipette to give standards of 0.5, 1.0 and 10.0 ppm Mg. 0.1% KCI was added to prevent ionic interference.

All stock solutions were stored in plastic bottles.

The above has discussed resistance to shrinkage of preforms exposed to 1260°C for 24 hours. This is an indication of the maximum use temperature of a fibre. In practice fibres are quoted for a maximum continuous use temperature and a higher maximum exposure temperature. It is usual in industry when selecting a fibre for use at a given temperature to choose a fibre having a higher continuous use temperature than that nominally required for the intended use. This is so that any accidental increase in temperature does not damage the fibres. It is quite usual for a margin of 100 to 150°C to be given. Accordingly this invention extends to use of the claimed fibres at elevated temperatures (i.e. at temperatures where the refractoriness of fibres is important) and not just to use at 1260°C.

In selecting a fibre a balance has to be struck between refractoriness of the fibre and saline solubility of the fibre. For example the applicants have found the best high solubility fibre (total solubility greater than 100ppm) is probably composition B7 as that has a shrinkage of 2.7% at 1260°C. In contrast the best refractory fibre is probably BZ-560 which has a shrinkage of only 2.1% at 1260°C but has a total solubility of only 27ppm. Although there are other fibres

with a lower shrinkage this fibre also has the property of retaining in large part its resilience on firing to  $1260^{\circ}$ C - many of the fibres become rigid after firing due to crystallisation and sintering. It appears that high levels of  $ZrO_2$  help to overcome this (BZ-560 has 7.64mol%  $ZrO_2$ ) but at the same time reduce solubility.

It will be evident from the above that incidental impurity levels are preferably kept as low as possible. The applicants surmise that as the various crystalline materials crystallise from the fibres impurities migrate to the grain boundaries and concentrate there. Thus a small impurity can have a very large effect.

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Comments																																									
Diopside/ Wollastonite	Natio				-																																				
SiO2 Excess	00 07	10.70	11.1	1 05	31.0	600	070	9 6	7.0	6.5	7.70	7 :	0.49	0.77	8.03	8.47	8.59	8.62	8.76	9.12	9.48	10.55	11.06	11.17	11.51	11.60	11.78	11.92	12.40	12.43	12.68	12.97	13 09	13.23	13 51	13 93	14 00	14.50	14.67	14.70	,
SiO2	36.61	51.15	2000	20.05	10 77	70 03	23.65	22.00	20.03	50.72	52.72	67.07	70.75	04.70	34.03	24.24	54.30	33.83	54.73	33.80	27.72	59.16	55.53	57.67	55.76	55.80	55.89	58.49	56.20	56.21	56.34	56.48	60.34	\$6.65	56.77	26 08	\$7.04	57.23	58.29	\$7.45	
3 TiO2	1693	10.0	5 12	0.30	17.0	807	8/ 0	2 ~	~~	220	(7 C	36	2.0	-		27.0	75.0	07.0	0.35	0.35	0.35	01.0	9.26	97.18	0.17	0.82		0.24	0.66	0.03	0.52	3.18	01.0	3.15	14	7.43	200		0.23	3.35	
mol% AI2O3	F			86.7									33		_				0.70						0.04 0.04			5.07	_	_	_								7.62		_
Composition MgO 2.4)2	F		_	7.76	_	26				_					7 0	0 9								_				_	70	77	85										_
Comp MgO	2	11.74		_		52 45.26		_		_			20 / 23			_			0.4							21.75				_	_	_	15 8.16		_				13.02		
CaO	58.	7 29.00		_	2	3.62			25.66	24.31	2		28.29		3	2 2	_	_	3/.//	_		_		_	2	77.7		_	36.13	37.0	34.2			34.4	24.48	38.5	35.08				200
Others	L		0.5					0.8				Ü	0				70		•			ì		\$. \$.				8.0					0.7						0.7		
SiO2	33.6	51.2	42.5	50.9	54.68	57.78	51.2	51.4	36.58	56.18	56.82	53.9	56	55.22	58.71	30 35	27.5	2003	× ×	20 25	20.30	200	7.00	8.76	61.38	29.83	29.05	7.7	57.74	37.54	57.57	62.36	57.3	58.39	60.32	57.38	59.82	63	56.7	58.2	8
TiO2																																									
wt% AEO3 TiO2	21.6	0.4	36.6	0.5	0.2	2.12	0.3	0.5	~	0.5	0.74	0.4	0.4		0.54	990	0.3	0.58	90	0 63	• •	6.0	2.40	2.5	16.9	<u>.</u>	•	5	(1.1)	0.00	0.91	0.33	0.3	0.27	0.25	0.73	0.13	0.7	<b>†</b> '0	0.0	0.48
22		10	0.2	10			15	671	0.05	0.05	0.05	14.8	5				15.1	1.46	2.7		15.2	000	20.5	7.0	00.0	Š	5	7.07			,	0.07	15.5	0.17	0.08	0.08	0.17	0.3	15.2		
Composition Mg() Zrd		<u>2</u> .	70	5.7	19.66	35.07	9.	~	17.05	16.81	17.36	5.1	97	0.77	19.74	13.01	9.9	111	•	77.0		X X/	,	, ,	7 7 7	9 6	7.0	,	.03	70.7	0.0	24.18	5.2	6.02	13.24	2.43	<u>5.4</u>	17.9	8.6	0.7	9.22
	50.8	27.1	19.7	32	70.05	3.0	22.2	26.5	26.62	24.45	23.92	23.8	27.1	12.79	18.48	26.29	161	36.07	31.8	30.5	22.8	18 50	31.2	C 2	3.07	3 6	2,7	7.07	34.00	25.59	32.7	9	20.7	33.1	24.28	36.62	34.34	18.8	17.1	39.1	28.15
	10.3		7 55	_				1.64		_		2	11.7		_	_	-		43.9		891	2	877	14.0			•	7,				:	9.77		_	_		6.9	21.3	_	_
				_	-		•		_		_					-				_			_			-												_		2.6	_
Shrinkage 1000C 1200C	10.7		515		/ / .	7.7.5	•	70.5	39.3	34.9	11.7	10.1	_	=	1.7	36.2	_	0.3		39.8	677	687	<u>.</u>	~ ~	2.0	2 0		2,7	, ,	+ 5	70.7	00.	χ, ·	9.	œ.	30.3	2.1	5.9	20.7	7.7	2.3
Shr 800C 100	0.0	36.6	2	<u>.</u>		2	70.7	÷			-	5.6	27.8	3 2			5.0	34.7	31.5	26.6	3.7	707	7.7	2		-,		o o		÷			7.7	<u>5.</u>	=		- !	2.8	7.6	<del>-</del>	_
· 🙀	0/9/0	11-79	02 C3	21.13	776	20,00	2.70	67-79	734	5/3	1/6	/7-79	01-78	208	112-19	.42-18	82-28	B3-3	6-28	B3.26	12-28	42-23	82-12	12.21	0.50	714	87.11	980	717	777 102 34	02-50	77.7	(7-29	594	AZ-11	63.21	260	88	52-22	271	B3-25

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	1	inknor			Composition	-	w1º 0				Compositi	١	ol%		٢	Sioz	Diopside,	Comments
Comp	800C 100	1000C 1200C	1200C	Q <sub>i</sub> S	Og W	20	Al2O3 TiO2	SiO2	2 Others	Q <sub>2</sub>	MgO ZrO	~	AI2O3 TiO2		SiO2	72	Wollastonite	
			-				11.0	٦	15.4	7, 7,7	1		80 0	ľ	57.16	-	Kallo	
586	<u>o</u> .	. o		35.00			2.0	\$ &	6 7	75.50		0 07	0.0		57.59	15.11		
- <del>-</del>	1	0. 2				0.47	0.20		64.72	8.56	33.37	0.27	0.75		57.71	15.41		
1757		3 6		19.78	•		2.57	- 9	.32	19.99	•	0.30	1,43		57.84	15.68		
969	, -1	03		30.9			0.21	28	18.1	32.68		0.12	0.12		58.04	15.96		
757	2.9			20.9			0.2	_	9.7	20.75			0.11		58.06	16.13		
12.34	6	3.4	_	9,0			0.23	vő	7.85	6.37		0.35	0.12		58.15	16.29		
A2.12	2.3	_		16.5		0.05	0.33	9				0.02	0.18		58.67	17.34		
RZ-19	23	7.		20			0.3		59.5 0.7	_		6.72	0.18		62.10	17.49		
A2-30	9	2.7		16.0			4.0	9	3.68	15.8			0.22		58.82	17.64		
A2-7		=		23.3			77°C	ç	86.	23.7		_	0.25		58.89	17.68		
80	1.7	2.5		5 /X.			0.2		54.4 0.2	_		_	0.11		58.84	17.69		
17.71	~	1.2	_	_			0.34	Ò	1.16	- 13.5		_	0.18		58.90	17.81		
R7.111	7	7.7		20.			0.2	_		0.4 21.42		3.41	0.12		29.09	17.93		
R7-137	. ~	90		0			0.2	_					0.12		09.09	17.95		
03-1		200		32.5			0.79	<u>ت</u>	0.11	34.36			91.0		59.21	18.02		
170	1 2	2 5		12.2			17.	<u> </u>	0.32	33.9			101		59.19	18.34		
D3-1A		7 0	_	2			0.3			0.7 21.47	_		0.19		62.57	18.36		
/+-7g				7			9.76	•	0 28	36.35		_	0.44		59.31	_		
		2 2	,				0.5			0.5 22.73			0 29		60.52	_		
7-79				. 0		0.1	0.2					0.05	0.11		59.34	89.8		
. (63			2 2				9.0			_			0.35		59.37			
017	] _						0.58	ç	1.62	26.35			0.33		59.36			
77-60	0 /	. ~	_	2.0			0.2	7 0					0.11	0.07	59.35			
719				_		5.1	0.5			0.7 28.69	59 7.80	2.50	0.30		60.71	18.91		
13.30	:						0.92		59.4	38.7	_		0.54		59.63		-	• •
A 7-0	0	6		21.			1.49	_							59.59			كنس
17-71	7.9	8.1		~		~	6.4			0.6 23.90	17.11	1.11			00.30	05.50		
R7-178	5.7		3.7	1.1			0.3			_	_	_			07.70			
BZ-106	~	8.2		92		6.4	0.2					5.00	77.0		26.30			
A7.76	2.7	161	~	19.7			0.7	_		0.6			7770		200.74			-
22		<u>-</u>		31.			0.05	_		32.49					39.83			
15.54	70	5.7		- 12		17.5	0.7			0.6 20.0		9.09			02.93			
275	;	9.0		28.				_		``			_		29.88	2.5		
02.20	×	7.8	_	_		5.1	0.3			0.6 22.10	10 14.21	2.42	0.17		01.10		_	
07 70	2 2	0 %	~	_		2	7:0			_	Ċ				61.13	_		
3 20	i ~	2 9		_			0.3	_		0.6 24.					_	20.21		
7.70		5	_	1.3			0.7	0.7	99	7				0.07	60.31	_		
070		9.9	_				0.3		60.3	17.					61.14	20.87		
82-412	. 2	3.2		6.3	19.2	77	0.2	 !	62.91.	51 20	_:	_;	_;	:	1 61.97	_		_

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Comments							-											2									ü					-	1.1%Fe2Os					-		100.11.00	0.4%Na20	1.32ava41.
idc' stonite	Katio	-			,												•																							`		-
SiO2 Excess	-	21.15	21.70	21.20	21 31	21 37	21.73	32.17	3. 1.	30.73	20.00	20.02	25.55	30.85	27.00	29.95	7.07	23.67	27.24	26.26	23.26	26.49	28.63	33.92	28.96	25.38	24.67	22.41	22.68	23.04	23.24	23.28	23.36	23.39	23.46	23.72	24.06	24 07	2 7	24 70	24.74	
SiO2	4/ 70	99	60.87	62.10	08.09	64.02	61.82	63.69	63 05	07 59	25.00	00.00	2	7	02.33	07.70	10.00	2//9	63.65	2 .	97.00	05.39	94.37	58.33	7.70	62.86	62.47	61.20	8	 84	61.62	3.5	61.64	61.69	61.73	61.50	62.03	2	3	62 31	62 43	1
TiO2								193	3.56	2.75	700	00.	. 30		0	0 :	7.7	3					9	0.08	0.08		1		0.70	9.0			0.07			0.73				0.07	0 07	;;
mol% A12O3 7	0.17	3.55	0.72	0.17	0.40	0.25	0.12	0.23	0.23	0.78	0 22	700	3 0	000	90.0	9.6	2.2	0.71	32.28	5.5	2.40	2.3	2 .	1.00	0.92	0.79	0.78	0.11	0.1	3	0.27	0.12	0.11	0.10	0.17	90.0	0.12	0.0	90	0.06	77.0	•
2	7 57	0.20	7.80	3.41	0.28	6.67	5.02	0.15	0.03	3.32	0 0	55		3.3.5	3.50	6.5	00.7	25.7	00.0	3 6	9 9	9 5	0.12	7.03	\$	1.59	0.28	8	19	G 13	8	80	0.37	90.0	0.28	2.65	0.54	5.33	0.42	2.49	0.14	
Composition MgO 2rC	14.57	1.02	15.07	14.25	3.42	7.47	14.61	7.26	7.20	7.43	7.16	15.13	X0 X1	78.71	76.07	7 36	17.70		07.0	0.00	2 2	, , ,	61.7	8 :	/4.7/	7.03	2	3.6	18.83	71.7	21.93	70.01	19.36	19.29	29.55	18.10	20.15	16.60	22.31	18.12	19.05	!
CaC	21.05	34.55	16.14	20.06	35.10	21.59	18.43	23.74	25.02	20.02	27.50	17 33	17.07	76.26	1,83	25.02	17 71	; ; ;	20.0	36.00	37.00	17.07	10.00	10.0%	12.70	7.77	76.97	5.5	10.57	10.43	9 5	3 :	6.50	18.8	8.26	16.96	17.15	15.98	14.89	16.95	18.29	1
Others	0.5		0.5	6.0		0.6	0.5	0.3	0.3	0.4	10	0.3	0.3	0 3	70	2	2	500	Š				, 0	÷ ;	3 6	5.0	0.0	2 6	7 6	7	Č	} :	5.7			0.3		0.5		0.7	9.0	
SiO2	63.2	59.54	39	63	61.71	61.3	61.8	1.79	64.9	64.3	64.3	67.6	7 99	6.17	7 99	79	3,0	20.5	77.79	20.00	72.29	* * * *	3			6.00	e co	8 8	2 5	1./0	60.1	7.60	0.00	03.09	67.62	63.3	65.33	62.4	66.67	64.6	8.99	
Ti02								9.9	4.8	3.6	2.8	2.7	2.7	27	,	0 /							0	7	3			•				-	7.0			_				0.7	0.1	1
wt°; Al2O3 TiO2	0.3	5.91	0.2	0.3	0.69	0.7	6	7.0	0.4	0.3	0.7	70						L									1				640	0	0.7	00	0.32	0.7	0.22	0.1	0.11	0.7	0.7	
ition Zr()2	]	0.41						0.3		6.7		5.3		2		3.3		L		_	_	_				9.0	ı											=	0.92	5.3	0.3	
Composition Mg() Zr	l	0.67					- [											L																•	•	12.5				12.6	i	
CaO	20.1	31.64	7.6	2			_													32.3	25.41	25.81				2 2	L							0.75						16.4	_'	
12600	"					· :		7.77		19.6	0; 	×.	8.6	97	5.2	29.5	7.2	67					11.1	٥			L				2.9	12.6	•		-	7.7		2.5	7.6	5.7	6.7	
1200C								_		_								L							30	3.2	2	77													· · · ·	
Shrinkag 1000C	3.9					7, 6			2, 0			9.8		7.7					21.6			7					=	=======================================			78		6 1			``	<u> </u>				:	
8000	1.6	15.3	2 .	;	5	9.0		3 5	š	-	0.0	0.5	0.0	7.7	0.0	0.0	0.0		18.8	3.3	4.3	_						0.7	1.6	6	=				`	_	_	0.7	1.7		į	
Comp	BZ-405	B3-3.4	B7_13	B1.11	82.45	87.4	RT.	RT. 2	1077.	D41.2	-10	710	110	9/0	sa	1-128	70	KW.1	B3-64	B3-2A	B3-5A	B3-4A	B2-440E	BZ-560F	9-1-28	BZA-3	98	2	B10	A2-10	BZ-59	B7D	A2-5	A7.31	2	3.5	A4-8	79	A2-13	BZ-440.1	B7A	

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	ć				ٽ	Composition	0,7,4 U	•			_	ပိ	Composition		mol;e		_	700	Diopside,	Comments
Comme	יאוניס	יוואלן יוווירן יאטאטן	.1 .3006	. 3000	0.0	CoM	3	A12(3) Ti(3)2		SiO2 Of	Others C	CaC	MgO Zr	2		TiO2 Si	Sicos	Excess	Wollasfonite	
روالية. د		: .		١																
R7.110C				8.7	16.2	12.6	5.3	0.1	0.1	64.3	L	16.82	18.21	251	90.0	0.07	62.33	24.74		0.6%Fe2O3
B7C				3.9	187	13.8	0.2	10		9.99	0.7	18.09	19.29	0.00	90.0		62.47	24.94		0.69%Fe2O3
BZ-1150K			_	6.4	15.5	671	7.5	0.7	0.1	63.9	8.0	16.27	17.38	3.58	90.0	0.07	62.63	25.33		0.6%tie 203
80	ί,	1.4	_	4.3	6.91	13.2	1.8	7.0	=	66.2	0.2	17.11	18.59	0.83	0.22	0.71	62.54	25.80		
0/8		1.5		3.6	13.9	16.8	0.7	0.7	0.7	68.7	0.7	13.65	22.95	0.31	0.05	0.07	62.97	26.00		
RZ-1150R				7.3	15.3	11.5	7.1	1.1	0.7	64.3	0.4	16.08	16.82	3.40	9.0	0.07	65.99	26.06		
R7-20	2	1.5		2.3	12.4	9.9	15.8	0.7		61.5	0.5	13.64	15.16	7.91	0.12		53.17	26.33		
200	- 2		2 0	2.7	1	17	8	0	_	67.B	0.2	17.91	18.24	0.36	0.17		63.33	26.65		
110	: -	2 2	7	. ~	3 4	¥	7	0.2	-0	9	0.2	15.63	20.65	0.18	0.11	0.07	63.36	26 79		
27 (15)	-	:	•	3			, ,	6		3 / 9	0 2	17 71	16.85	\$7.	0 1 2	0.07	07.69	26.87		(1/21/1/28) (1
1057-750						: :	7 5		Š	6.43	. c	14.5	11.00		: =	À.	23.63	27.05		Name and the
0+179	) j	7.	? ;	7.7		- :	7	• •	-	2	3 6	0.01		7	5	5	3 3	37.76		
BZ-4150	_	<u> </u>	7.7	3.2	15.2		7.		- -	200	2 0	0.00	10.7	2 0	9 :	) 6	2 5	27.10		
70	8.0	Ξ	2.3	3.5	15.4	11.6	œ.	0.2	_	65	0.3	16.10	16.87	2.76	5	0.73	7	80.77		
BZ-437	0.7	0.0		7	15	11.2	6.1	0.		65.7	0.3	15.60	17.66	5.83	<b>.</b>	-	63.79	27.59		
47-13					197	22.85	101	0.25		70.07		4.50	31.05	0.45	0.13		63.86	27.72		
07.61	0	7	1.7	161	10.4	6.6	17.6	0		61.4	9.0	11.71	15.36	8.93	90.0		63.93	27.86		
5550	3 6		:	:	1		-	-	0	169	0.2	14.14	21.47	0.05	0.05	0.02	64.22	28.51		
191/	5	-		4		10.26	80	0, 0	_	68.65	-	8	26.90	0.45	0.16		64.34	28.67		
07-7W	-	?		3 6	-		7	-	0.1	61.6	0.4	13.31	14.00	7.69	0.62	0.08	64.31	28.69		
BZ-Sout	_	-		?	1 59	16.57	9	- P	<u>.</u>	68 19		11.71	23.30	0.42	0.22		64.35		_	
A2-20	- ;			).(	17.4		13.6	-		63.5	9.0	13.58	15.12	6.73	0.18		5.13			
85.30 150	7			:	17.15			}		EE 89		17.67	17.75				64.58			
739					7.1	77.31	1 23	91.0		71.24		4.34	30.23	0.55	0.10		64.77	29.55		
67-74	_	0.		5.7		0	2		0.7	623	7.5	13.37	11.11	7.66		0.08	64.79			196Na20
2006-79				; (	-		7 7	-	2	62.7	0.0	12.98	14.05	7.88	90.0	90.0	2.3	29.97	_	
B2-304.		71	3.6			10,0	10.2	50	-	65.2	0.5	14.00	15.76	36.	0.18	90.0	65.03		<del>-</del>	
010-70		2	•				¥.	0	0	62.5	0.8	13.05	14.12	7.61	900	0.08	65.07	30.22	-2	
27.860		-	3				15.1	0	0.1	67.9	0.5	13.01	13.92	2.5	0.08	0.08	62.29		2	
200		: :				12	1.87	0.1	0.9	68.2	0.2	16.26	17.07	0.87	0.08	0.65	65.10			
B7.56	-			22	9		15.7	0.1		63.7	0.5	11.47	15.03	7.88	0.06		65.56		-	
27-17	1 2	1.2					101	0.24	_	71.14	•	6.70	27.03	0.45	0.13	_	69.69		<b>20</b>	
17-77	0.2		7	7	13.2	9.7	=	0		65.6	0.4	14.20	14.51	5.38	0.06		65.85		0	
47.6					15.17	_	1.13	0.07		69.29		15.46	18.09	0.52	3.0		_		0	
3	0	0.8		3.5			5.7	0.7	_	67.3	0.3	14.24	16.46	2.72	0.06	0.74		_		
11. Kn	4			1.7			18.2	0.		63.1	7.0	9.12	15.19	9.32	9.0	_	66.30	32.61	_	
162.37	;						0.36	0.23		73.09		6.23	26.70	0.16	0.12		66.79		6	
A2.17		13			11.58	14.52	1.58	0.15		70.43		11.78	20.55	0.73	0.08		98.99		- 5	
A2-22		Ξ			9.36		0.83	0.33		71.48		9.42	22.88	0.38	0.18		67.14	_	<b>30</b>	
117.63	03	8.0		2.4			8.6	0.1		67.4	7.0	2.3	14.56	4.18	0.06	-	67.20			
8Z8	0.4		_	2.7	71:	9.9	10.8	0.2	-	67.8	0.5	12.19	14,73	5.26	0.12		I 67.70	35.39	16	

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Table 2 .... (sheet 5)

Comments			2		0.496.Va2O					0.390 Va2O														•													ы		
SiO2 Diopside: Excess Wollastonic	Rutio																																					464.59	47.59
SiO2 Excess		37.75 42.65	46.20	22.10	22.50	22.54	22.90	23.65	24.35	24.36	24 76	25.21	25.53	25.64	25.78	26.22	26.22	26.33	26.40	26.71	26.85	27.04	27.60	28.53	28.98	29.21	29.40	29.49	29.74	30.37	30.90	30.98	31.19	32.43	32.63	32.93	36.23	25.33	26.82
SiO2		68.88	73.10	62.50	62.40	æ	62.72	62.25	62.33	63.12	<b>S</b> .3	83.58	65.67	63.26	G. 12	63.34	63.21	54.11	63.86	63.47	65.75	64.43	63.85	65.21	65.03	65.33	65.54	67.40	67.22	68.89	66.02	67.34	66.24	86.65	68.88	67.16	88.9	65.76	2 2 3 3
TiO2		•															0.02																0.07						
mol% Al2O3		0.0	0.08	0.12	71.0	6.5	7 .	7170	9 :	0.12	0.12	0.12	0.12	90.0	0.17	0.35	0.57	<b>G</b> 11	0.12	0.40	0.19	0.11	0.11	0.12	0.29	0.06	Q.11	Q.12	0.19	0.29	90	0.13	Q.11	0.17	0.18	0.11	3	0.12	0.12
		1.06	0.80	3.12	2 5	3.5	3 5	3.40	9.5	* ;	3.17	3 3	7.00	\$25	2.57	2.52	1.45	3.23	4.19	1.46	9.06	2.76	2.56	2.58	3.34	3.15	2.19	6.38	7.78	2.72	2.57	9.13	1.12	3.38	\$36	1.70		3 ;	19:1
Composition MgO ZrO2		14.61	23.93	14.23	2	14 17	76.75	16.30	91.51		70.0	7	3.	7	- -	∓ 19:	17.07	17.38	14.60	17.11	7.85	14.83	16.63	14.16	14.58	14.28	14.39	7.74	7.72	7	3	26.	14.31	14.16	7.65	14.13	27.28		14.04
CaO	70 01	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	7.08	70.03	10.69	10 14	2	8	18 10	2 0	; ;	100	7.6	10.35	3.6	17.36	17.63	18.16	17.24	17.57	17.18	18.17	16.8T	17.94	16.76	17.18	17.76	18.36	17.10	6.5	16.82	5.5	3.	13.69	17.93	8.	20 10	10 00	17.69
Others	T		ļ	3 ~		7	-	č	0	ò		7 0	9 6	3 6	0.0	0.7	0.4	7	9.0	4.0	0.7	0	0.0	<del>-</del>	0	0	7	9.0	9.0	? 5	3 6	9 6	3	3 6	2	0.3	3	3 6	0.3
SiO2	77.75	73.43	/0.8/ /	6.0	809	64.2	63.5	61.2	63.2	7	3	3 5	3 5	2.5		3 3	65.7	65.8	3	65.8	61.2	. <del>.</del> .	63.8	9.99	66.5	8.99	67.7	ż	3 5	4.6	2.7	0.70	8	? .	7.	60 5	2 2	3	8
102			Ì						-								 O	,				•				_			_			-	- -				Ť		_
wtº.o Al2O3 TiO2	Ē	0.0	6,13	0.2	0.3	0.7	0.2	0.1	0.2	0.7	0.7	2	-		3	٠ . خ	- ;	7.0	0.7	) c	2 6	7.0	0.2	0.2	0.5	5.5	7 6	7 0	3 8	3 6	3 6	2	, ,	3 5	3 6	7.0	5	0.7	0.2
3	124	2.23	2 3	. ~i	15.4	7.4	6.7	13.3	8.5	9.9	7.7	13.7	10.7	7		7		0 0	9 -	7.5	C. 7	ė.	'n	'n	,	0.0	9 9	0.71	·	ì	, ,	7	, "	2	· ·	9 4	222	7	7.
Composition Mg() Zr	12.35	10.09	0	6	S	9.8	11.2	9	7.6	9.1	6.6	4	6	6	-	? .	- 0	, c	, <u>.</u>	-	, -		?		2 2	0 0		7	6	÷ =		ç	0	<b>Y</b>	0	0 W	8	9.4	9.7
0.00	12.67	12.4	0	17.8	17.4	18.5	17.2	14.5	17	18.4	17.5	17,3	15.4	18.2	7 7	2 -			1.0	- 0		16.3	7.01	1./1	9 7	7 (	3 71	7	3	4	13.4	16.4	3	1 7	7	14.8	18.1	18.1	13
1260C			7,6	7	2.2	2.8	2.9	3.3	3.7	3.3	1.9	. 3.1	2.3	2.7	-	?	~	, ,	•	2	3.4	, ,	; ;	3 5	7 .	9 9	-	6	1	6	0	6	7.4	=		1.	-	2.7	2.2
:00C								2.3			1.7	!				, 7			26	1 2	:			:			0.7	-	,			-	2.9						
Shrinkage 1000C 12	Ξ	0.7	2	8.7	Ξ	2.1	6:1	7.8	1.7	Ξ	Ξ	Ξ	1.8	7.	7		-	. 7	:	0.7	-	=	=	2 5	} =		6	0.5		1.2	0.5	13				9.0	6.0	1.1	1:1
8000.			-	0.7	0.7	Ξ	<u> </u>	=	0.8	9.0	0.3	7.0	9.0	0.7	0.3		0.7			0.3	50	17	90	9	9 0	90		0.3	0.5	0	0.3	0.5	0.7	0.3	_	0.7	0.2	90	0.7
Comp.	A2-15	A2-16 A2-28	10t-28	BZ-429	61.79	82413	8558	82.53	0£t-28	82768	BZ-11	BZ-S0	BZ-62	BZ~101	BZ-43S	BZA-5	BZ~409	10-28	BZA-4	95-78	BZ-403	BZ-433	BZ-400	BZ-415	BZ-410	8Z-419	BZ-36	BZ-48	BZ-4	BZ-401	BZ-52	0ZF~Z8	BZ-44	82.7	BZ-426	BZ-438	BZ-35	BZ-402	BZ-425

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Table 2 .... (sheet 6)

###. 800C 100C 1200C 1200C CaO    0.5			Shrinkage		Γ		1.2		WT. o		1	_		position	1	1				_	Comments
13	Сսուր.		1000C	20.05	360C	_	Og M		1203 Tic					20	~					ollastomte	
1,	877.78	5 ()			, S	18.3	101	17	0.2	-	66.8	┸	L	L	156.7	0.11	F	1_	-	ı	
12	97-71		60		4.7	19.3		5.2	0.2		64.7				2.47	0.11			19:61	20 69	
1,	RZ-16	1.2			6.1	19.2		5.7	0.3		5.3	_	_		2.47	0.17	_		23.99	19.75	
1	3ZA-2			2.8		18.5		9.0	=		66.4	_	_		0.28	0.56	_	_	25.86	18.86	
10   10   11   12   13   13   13   13   14   14   14   14	3ZA-1			2.6		18.5		0.6	9.0		1.19		_		0.28	0.33			26.63	18.86	
1	32-160	9.0		7	3.1	19.3		S.	0.3	<u>.</u>	8.19	``	_		2.42	0.17			23.88	09.91	
1.0		_		~	2.7	18.8		0.7	0.7		8.99	_	_	_	0.32	0. II.			26.21	15.80	
0.1         1.9         3.6         1.0         3.6         1.0         3.6         1.0         3.6         1.0         3.6         3.7         3.1 <td>7777</td> <td>-</td> <td></td> <td></td> <td>2.4</td> <td>18.4</td> <td></td> <td>3.5</td> <td>0.7</td> <td></td> <td>67.1</td> <td>_</td> <td></td> <td>14.27</td> <td>1.65</td> <td>0.11</td> <td>_</td> <td><b>6.</b>30</td> <td>28.15</td> <td>12.77</td> <td></td>	7777	-			2.4	18.4		3.5	0.7		67.1	_		14.27	1.65	0.11	_	<b>6.</b> 30	28.15	12.77	
1,	87.70	6	:	6.7	3.6	18.1		10.2	6.0		64.8			7.67	5.12	0.55		66.70	28.29	9.73	
0.2         1.3         9.1         9.8         3.5         0.2         0.2         1.1         1.4         0.2 <td>217.78</td> <td></td> <td>_</td> <td></td> <td></td> <td>_</td> <td></td> <td>=</td> <td>0.2</td> <td></td> <td>1.99</td> <td>_</td> <td></td> <td>13.97</td> <td>1.93</td> <td>0.11</td> <td></td> <td>63.89</td> <td>25.85</td> <td>8.93</td> <td></td>	217.78		_			_		=	0.2		1.99	_		13.97	1.93	0.11		63.89	25.85	8.93	
1	10 / N	2			3.1	_		3.5	0.7		6.99	7.0		14.07	<u>i</u>	0.11		9T.79	27.27	90	
0.7         1         3.2         19         8         10.4         0.4         65.8         5.4.3         0.4.4         65.8         26.4.3         737           0.9         0.9         1.6         10.4         20.2         6.5         0.4         10.0         1.4         0.1         64.8         26.4         0.1         0.0         1.4         0.1 <td< td=""><td>70 70</td><td>_</td><td>,</td><td></td><td></td><td>707</td><td></td><td>4.3</td><td>6.0</td><td></td><td>64.7</td><td>0.5</td><td>_</td><td>14.12</td><td>2.03</td><td>0.57</td><td></td><td>62.53</td><td>23.04</td><td>7.88</td><td></td></td<>	70 70	_	,			707		4.3	6.0		64.7	0.5	_	14.12	2.03	0.57		62.53	23.04	7.88	
0.9         0.9         1.6         19.1         9.9         3         0.2         66.7         0.5         19.7         14.26         14.1         0.11         66.45         27.8         7.1         0.11         66.45         27.8         7.1         0.11         66.45         27.8         7.1         0.11         66.45         27.8         7.1         0.11         66.45         27.8         7.1         0.11         67.1         27.1         67.10         0.11         67.1         27.1         67.10         67.1         27.1         67.1         27.1         67.1         27.1         67.1         27.1         67.1         27.1         67.1         27.1         67.1<	174.70		_		3.2	13		10.4	7.0		8.09	9.0		7.69	5.23	0.24		65.83	26.43	73.7	
0.9         1.8         1.0 d         2.0 d         6.5 d         0.4         20.0 d         11.2 d         1.70 d         0.11 d         0.7 d         1.71 d         1.12 d         0.11 d         0.7 d         0.11 d         0.12 d </td <td>120</td> <td>÷ =</td> <td></td> <td></td> <td>2.6</td> <td></td> <td>5</td> <td>٣</td> <td>0.7</td> <td></td> <td>66.7</td> <td>0.5</td> <td></td> <td>14.26</td> <td>1.41</td> <td>Q.11</td> <td></td> <td>61.45</td> <td>27.48</td> <td>7.36</td> <td></td>	120	÷ =			2.6		5	٣	0.7		66.7	0.5		14.26	1.41	Q.11		61.45	27.48	7.36	
0.0         1         14         2.1         18.3         5.1         8.6         0.2         17.10         0.07         0.11         0.07         0.11         0.07         0.11         0.07         0.11         0.07 <td>77-75</td> <td>-</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>3.6</td> <td>0.2</td> <td></td> <td>65.3</td> <td>0.7</td> <td>_</td> <td>14.12</td> <td>1.70</td> <td>0.11</td> <td></td> <td>63.14</td> <td>24.58</td> <td><del>1</del>19</td> <td></td>	77-75	-						3.6	0.2		65.3	0.7	_	14.12	1.70	0.11		63.14	24.58	<del>1</del> 19	
0.0         0.4         2.2         18.3         5.1         8.6         0.3         66.5         0.6         17.5         4.28         0.18         67.80         31.33         5.42           0.6         1.7         6.7         6.3         0.6         22.16         1.7         0.4         6.48         2.8         3.2         2.2         1.8         3.2         2.2         3.2         2.2         1.6         0.7         0.4         0.4         0.4         0.6         2.1.16         1.7         0.7         0.4         0.2         0.7         0.7         0.2         0.7         0.7         0.2         0.7         0.7         0.2         0.7         0.7         0.2         0.7	77-77	5	-		3			9.0	0.2	0.7	65.6	0.3		17.10	0.27	0.11	0.07	61.17	22.14	585	,
0.1         0.1 <td>113</td> <td>5 6</td> <td></td> <td></td> <td>,</td> <td></td> <td></td> <td>98</td> <td>0.3</td> <td></td> <td>66.5</td> <td>9.0</td> <td>_</td> <td>7.75</td> <td>4.28</td> <td>0.18</td> <td></td> <td>67.80</td> <td>31.33</td> <td>5.42</td> <td></td>	113	5 6			,			98	0.3		66.5	9.0	_	7.75	4.28	0.18		67.80	31.33	5.42	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	15.25					1		9	70	r	63.4	9.0	┡	7.62	5.14	0.24		98.79	24.58	5.22	
1, 1         20, 7         20, 7         20, 7         20, 7         20, 7         20, 7         20, 7         20, 1         10, 1         0.0         63, 2         10, 1         0.0         63, 2         10, 2         20, 1         10,	05-75	5 6			`	20		5.5	0.7		65.7	9.0	21.16	11.78	2.65	0.12		64.30	25.94	S. 18	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25-437	· ·			20		≈0	5.6			63.5			12.24	2.70			62.81	22.92	4.82	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	22.4340	_			_			3.2	0.3	_	64.2	0.5		14.16	1.51	0.17	ţ	62.24	22.97	2 .	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	75-37			_		20.3			0.2	0.7	97.1	0.5		16.02		0.17	0.07	03.28	3 8		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	97.42	•		_		1 20.3		8.2	0.3		30	9.0		7.58	7.06	0.18		00.07	30.87	4 r	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	60.20	_			2	22.8	_		0.3	0.7	64.8	0.7	23.28	74.49	0.23	7.5	/0.0	07.70	00.00	9.70	
0.8         1.1         21.28         9.34         0.54         0.52         66.17         22.04         1340         0.22         0.30         27.02         27.19         27.19         27.19         27.19         27.10         27.19 <td>97.44</td> <td>0</td> <td>7.7</td> <td></td> <td>_</td> <td>5 22.2</td> <td></td> <td></td> <td>0.3</td> <td></td> <td>63.2</td> <td>9.0</td> <td>24.17</td> <td>7.42</td> <td>70.7</td> <td>0.78</td> <td></td> <td>77.70</td> <td>27.43</td> <td>7.7</td> <td></td>	97.44	0	7.7		_	5 22.2			0.3		63.2	9.0	24.17	7.42	70.7	0.78		77.70	27.43	7.7	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	R3-22	0				21.28		_	0.52		66.17	-	22.04	13.40	0.23	0.70	0.07	62.50	37 10		
0.2         13.26         9.33         0.3         0.56         64.09         24.10         13.49         0.14         0.32         0.56         64.09         24.10         13.49         0.14         0.35         0.27         69.42         38.47         2.26           0.7         0.8         20.98         7         0.79         0.78         68.56         21.97         0.36         0.27         69.42         38.47         2.26           0.7         0.8         20.98         7         0.79         0.78         68.56         21.97         0.48         66.240         28.94         1.59           0.7         0.8         0.7         0.6         25.88         0.77         25.81         11.48         2.5         0.48         1.59           0.6         0.3         27.14         6.5         0.49         65.11         1.78         27.12         1.84         1.77           0.6         0.3         27.14         6.5         0.49         65.11         1.78         27.12         1.84         1.59           0.6         0.3         0.4         6.5         0.4         65.11         1.78         27.12         1.84         1.77         1.79	821	Ö			7	1 22.3			0.2	0.7	67.7	7:0	87.77	13.70	0.40	0.0	3	00.19	73.83	2.5	
0.2         18.74         7.03         0.75         0.47         7.03         2.03         7.03         0.75         0.74         7.03         1.25         0.73         0.74         7.03         1.25         0.73         0.74         7.03         1.25         0.73         0.74         7.03         1.25         0.75 <th< td=""><td>B3-23</td><td></td><td></td><td></td><td></td><td>23.20</td><td></td><td></td><td>0.56</td><td>_</td><td>64.09</td><td>-</td><td>10 68</td><td>10.43</td><td>9.0</td><td>0.32</td><td></td><td>69.42</td><td>38.47</td><td>22</td><td></td></th<>	B3-23					23.20			0.56	_	64.09	-	10 68	10.43	9.0	0.32		69.42	38.47	22	
0.7         0.8         20.36         20.37         0.79         0.6         25.84         7.47         2.54         0.18         63.94         25.34         1.94           1.2         1.3         2.4.13         5.2         0.3         65.77         26.11         11.48         2.54         24.81         1.78           0.4         2.5.69         8.12         6.5         65.77         26.11         11.48         6.2         24.13         1.59           0.6         0.3         27.26         8.12         0.6         65.03         65.03         6.30         6.2.13         24.13         1.50           0.6         0.3         27.26         5.33         0.61         0.58         65.11         26.50         82.0         0.30         64.66         29.03         1.50           0.0         0.3         0.4         29.79         5.44         0.6         65.08         25.16         5.55         0.23         63.04         27.28         1.31           0.5         0.4         24.91         3.76         0.43         66.42         25.16         5.55         0.25         68.80         37.28         1.31           0.2         0.4         24.91	B3-28				_	18.7-		67.0	0.47		6.0.0		71 97	10.20	0.38	0.45		10.79	33.64	1.9	_
1/2         1/3         9         23/14         25/14         25/14         26/14         27/14         26/14         27/14         26/14         27/14         26/14         27/14         26/14         27/14         26/14         26/14         27/14         26/14         26/14         26/14         26/14         26/14         26/14 </td <td>B3.27</td> <td>Ö</td> <td></td> <td></td> <td></td> <td>`</td> <td>× •</td> <td>0.79</td> <td>9 ~</td> <td></td> <td>8 2 8</td> <td>90</td> <td>25.88</td> <td>7.47</td> <td>2.54</td> <td>0.18</td> <td></td> <td>63.94</td> <td>25.34</td> <td>1.9</td> <td></td>	B3.27	Ö				`	× •	0.79	9 ~		8 2 8	90	25.88	7.47	2.54	0.18		63.94	25.34	1.9	
0.5         27.14         6.51         6.523         27.72         9.87         0.23         62.18         24.13           0.6         0.3         27.26         5.34         0.61         0.58         65.11         26.50         8.20         0.30         63.46         29.03           0.6         0.3         27.26         5.33         0.61         0.58         65.01         28.56         7.77         0.03         64.66         29.03           0.5         0.4         29.79         5.44         0.47         0.43         62.61         31.10         7.90         0.03         61.00         22.01           0.5         0.4         24.91         3.65         0.45         64.66         5.55         0.23         0.25         65.03           0.5         0.4         0.47         0.43         64.61         5.55         0.23         0.25         68.80         37.38           0.5         0.49         0.45         0.45         66.61         37.36         67.39         67.39         67.39         67.39         34.45           0.9         0.8         0.6         0.9         0.6         0.6         0.6         0.6         0.6         0.6	BZ-15		1		1	_	1		3	T	65.77	T	26.11	11.48				62.40	24.81	1.7	<b>80</b>
0.4         27.11         2.57         0.58         65.11         26.50         8.20         0.34         64.66         29.03           0.6         0.3         27.26         5.34         0.61         0.58         65.08         28.56         7.77         0.03         63.64         27.28           0.5         0.4         29.79         5.44         0.47         0.43         66.61         31.10         7.90         0.03         63.64         27.28           0.5         0.4         23.7         3.76         0.43         69.42         25.16         5.55         0.23         0.25         68.80         37.38           0.5         0.4         24.91         3.65         0.45         66.78         26.61         5.42         0.32         0.25         68.80         37.38           0.2         0.3         1.71         1.03         0.65         0.45         66.78         27.06         2.86         67.78         67.03         0.39         69.47         38.44           0.9         0.8         0.91         0.55         0.93         0.33         3.39         62.38         0.33         62.98         25.51	719	_				27.6				_	65 23		27.72	9.87	0.23			62.18	24.13	<u>. 5</u>	
0.6         0.3         27.26         5.33         0.06         65.08         28.56         7.77         0.03         63.64         27.28           0.5         0.4         29.79         5.44         0.47         0.43         62.61         31.10         7.90         68.80         37.38           0.4         23.7         3.76         0.43         69.42         25.16         5.55         0.23         0.25         68.80         37.38           0.5         24.91         3.65         0.65         0.45         67.58         26.61         5.42         0.32         0.26         67.39         34.45           0.2         0.3         1.71         1.03         0.65         68.74         27.06         2.58         0.31         69.47         38.44           0.9         0.8         30.62         2.06         0.91         0.55         62.33         33.14         31.10         0.45         0.39         62.78         25.51	718		<u>.</u>			2.01.0			0.58		65.11		26.50	8.20	0.30	0.34		64.66	29.03	<u>~</u>	
0.5         0.4         29.79         5.44         0.45         0.42         25.16         5.55         0.25         0.25         66.00         22.01           0.5         0.4         29.79         5.44         0.47         0.43         69.42         25.16         5.55         0.25         68.80         37.38           0.4         24.91         3.65         0.45         67.58         26.61         5.42         0.32         0.26         67.39         34.45           0.2         0.3         24.99         1.71         1.03         0.65         68.74         27.06         2.58         0.51         0.39         69.47         38.44           0.9         0.8         30.62         2.06         0.91         0.55         62.33         33.14         3.10         0.45         0.33         62.98         25.51	B3-14					27.7			90.0		80.59	•	28.56	7.77	_	0.03		63.64	27.28	<u>.</u> .	_
0.2         0.3         3.76         0.47         0.43         69.42         25.16         5.55         0.25         68.80         37.38           0.3         24.91         3.65         0.65         0.45         67.58         26.61         5.42         0.32         0.25         67.39         34.45           0.2         0.3         1.71         1.03         0.65         68.74         27.06         2.58         0.39         69.47         38.44           0.9         0.8         30.62         2.06         0.91         0.55         62.33         33.14         3.10         0.45         0.39         62.98         25.51	7 2			2 2		29.7		,			62.61		31.10	7.90				61.00	22.01	÷	-
0.2         0.3         24.99         1.71         1.03         0.65         67.38         26.61         5.42         0.32         0.26         b).39         34.42           0.2         0.3         24.99         1.71         1.03         0.65         68.74         27.06         2.58         0.51         0.39         69.47         38.44           0.9         0.8         30.62         2.06         0.91         0.55         62.33         33.14         3.10         0.45         0.33         62.98         25.51	91 20	-		777		23		_	0.43		69.42		25.16	5.55	0.23	0.25		68.80	37.38	2	
0.2 0.3 24.99 1.71 1.03 0.65 68.74 27.06 2.38 0.31 0.39 0.34 3.04 25.51 0.99 0.55 62.33 62.33 62.33 62.38 25.51	R3-10		6			. 24.9					67.58	_	26.61	5.42	0.32	0.26		66.39	30.40	7 -	<u> </u>
0.9 0.8 0.91 0.55 2.06 0.91 0.55 62.33 33.14 3.10 0.92 0.90 0.50	R3.16					24.9					68.74		27.06	2.58	0.51	0.50		77.60	25.54	= =	
	B3-13	0			_	30.6	_			_	62.33	-	33.14	01.5	0.45	CC.0		04.70	10.04	:	<b></b>

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Comments		_										
Diopelide	Wollastonite	Ratio	-		9	102	ž	201	20:1	20.1	6 6	.02
Sio	Excess		L									28.89
	SiO2		67.73	65.22	57.73	73.37	68.47	65.20	65.52	09 89	9 19	64.52
mol%	AIZO3 TiO2		0.42	0.27	0.17	0.18	0.24	0.29	0.23	0.29	0.29	0.38
ioi	ZrO2		0.28	0.25	0.05	0.35	0.50	0.34		0.15	50.0	0.14
Composition	. OgM		2.79	2.63	2.92	0.97	0.74	0.89	1.47	0.89	0.88	0.55
	CaC		28.79	31.64	32.59	25.13	30.10	33.27	32.77	35.08	37.18	7
Γ	Others				0.3				0			
	SiO2		67.25	65.86	65.5	73.28	67.59	65.3	÷.99	64.1	62.3	요 공.
490	Alzos Tioz		0.7	0.47	0.3	0.31	0.4	0.5	0.4	0.5	0.5	700
ı	ZK)2 /		0.57	0.51	<u></u>	0.72	10.1	0.7		0.3	0.1	0.28
ompositi	MgC		98.1	1.78	7	_	_	9.0			9.0	0.37
	C <sub>E</sub> C		20.08	29.82	ñ	23.43	27.76					31.93
	1260C				3.2				1.8	13	2.2	
	1200C							Ξ		7		
Shrinkage	1000C 1200C 1260C		50	6.0			0.7	<b>1</b> .0				9.0
	၁၀							0.5		0.6	0.5	
	Comp.		23-17	B3-15	E32	B3-32	83.31	E25	13	E34	E23	B3-30

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Table 3 .... (sheet 1)

Comp.	Cac	OgM	Zr0.2	Alzo3 Tio2	SiO2 (	Others	Cac	MgO 2.rc	~	AI2O3 TiO2	SiO2	CaO	MgO	SiO2	Total	Excess
	ŀ		ŀ													
7:11:2	2.9	0.0	0.7	11.5	7.76	0.2	3.87	0.78	0.00	37.78	93.93					
	19.7	+ 0	0.2	366	12.5	0.5	24.58	0.09	0.11	25.12	49.50	5		13	≈	
210	50.8			24.6	23.6		58.82			15.67	25.51	30		0		
83-3.1	31.64		110		59.54		34.55	1.02	0.20	3.55	89.09	25	2	30		-274
2.1	32.3	0.48	0.12		60.83		35.08	0.73	0.06	2.48	99.19	19	2	58	_	
51	17.6		17.5	0.2	59.1	0.0	20.08	7.78	60.6	0.13	62.93	20	'n	12		
9	14.9		17.3		61.2	0.7	17.15	7.85	9.06	61.0	65.75	6	6	91		
.Sz	13.4	S	17.5		62.8	9.0	15.39	7.99	9.15	0.13	67.34	7		=		
<b>\$</b>	15.1	4.9	15.1		63.6	9.0	17.10	7.72	7.78	0.19	67.22	9	"	_	28	-0.25
12	18.9	~	153	0.3	50	0.7	21.47	7.90	7.86	0.79	62.57	11	~	17		
15	22.3	2	15.2		\$6.4	0.7	25.06	7.82	7.77	0.19	59.16	11	•	26		<b>.</b>
27	26.5	~	071		51.4	8.0	29.95	7.86	7.66	0.31	54.22	17	~	23		
-10	17.4	5.1	15.4	0.3	8.09	9.0	19.68	8.02	7.93	0.19	64.18	œ	6	77		
B3-31	27.76		10.1		07.59		30.10	0.74	0.50	0.24	68.42	Š	7	112		
25	20.7		15.5		57.3	0.7	23.35	8.16	7.96	0.19	60.34	8	<u></u>	76		
2	1193	0.37	0.28	30	2.5		7	0.55	0.14	0.38	64.52	83	<u></u>	163	240	0.04
77	23.8		11.8		53.9	0.7	27.00	8.05	7.64	0.25	57.07			22		
۔۔	31.1		0.7		65.3	0.5	33.27		0.34	0.29	65.20	20		*	136	
90	36		0.17		59.4		38.72		0.08	0.54	59.63		~	201		<u>.</u> .
22	23.43		0.72		73.28		25.13	0.97	0.35	81.0	73.37	×	×	×	×	
	33		0.3		7.79	0.5	35.08		0.15	0.29	63.60			115		
	35.1		0.1	0.5	62.3	0.5	37.18		0.05	0.29	61.60			13.		0.54
15	19.3		131		61.3	0.0	21.59		6.67	0.25	64.02		~			
2	37.1		1.0	9.0	60.2	0.5	39.20	1.03	0.05	0.35	59.37			16.		
_	39.1			9.0	58.2	0.5				0.35	57.35	58		225	283	
5	17.3		13.7		62.7	9.0	_	7.80	7.00	0.12	65.67		S			
07	20.9		13.2	0.3	59.5	0.7	23.37	7.62	6.72	0.18	62.10		<u>.</u>	~		_
~	42.79	0.77			55.22		11.85	1.12		-	54.03		7	16		
BZ-36	16.5		12.6		64.9	9.0		7.74	6.38	0.12	67.40		m	91		
_	31	_			66.4					0.23	65.52					
35	18		12.2		63.2	0.5					65.76					
91-	24.99		1.03		68.74		27.06		_		69.47	27	2			
-29	181		10.2		8.79	0.0					66.70	10				
-	26.68		0.57		67.25		28.79				67.73	64	=			
<u>.</u>	29.82		0.51		98.59		31.64				65.22		_	15.		
17	16.3		10.7		67.1						<b>88</b> .	=		77	39	<b></b>
82-5	22.1	6.4	10.3		8.09	9.0			5.18	0.18	65.69		_	~		3 2.17
717	19		10.4		8.63.8						65.83	=	<u></u>	78		
RZ-30	20.2	~	10.3		63.4	90	27 14				64.86			~	34	
					-		_				-				_	

Table 3 (cheet 2)

	L	Composit	. =	wto o					Compositi	1	nol <sup>9</sup> o				Solubility			MgO
Сошр	င္မ	MgO	ZK 12	VI203	T:02	SiO2	Others	CaO	MgO ZrOZ		Alzo3 T	Ti02	SiO2	CnO	MgO	SiO2	Total	Excess
83-13	30.62	ļ	L	1_		62.33		33.14		0.45	0.33		62.98	=	7	151	g	12
BZ-13	32	5.1	or _	0.5		50.9	0.7	35.00		4.98	0.30		51.96	38	12	5	6	3.18
E32	<u>.</u>					65.5	0.3	32.59		0.03	0.17		64.27					2.70
83-11	33.25					61.71		35.10		0.28	0.40		08.09	28	15	162	205	2.74
B3-9	34.49					60.28		36.35		0.24	7.0		59.31	00	2	175	188	2 99
83.21	36.62					57.38		38.96		0.01	0.43		\$6.98	25	9/	175	216	* 13
18.28	22.2	_				63.2	0.0	24.17		10.1	0.18		64.22	35	/3	76	7	3.73
8231	<u> </u>					66.5	9.0	19.99		4.28	0.18		67.80	13	-	-	9	3.70
82-33	20.3					8	9.0	22.11		7.06	0.78		66.07	7.		} ≈	<b>2</b>	2 2
B3-64	24.83					63.24		26.57		0.07	3.35		63.17		2	2 ×	2	27.
B27-3	19.2		6.7		3.6		7:0			3.32	0.78	2.75		9/	7	20	2 6	202
B3-5.4	25.41					63.74		27.07		0.28	2.33			Et	- 1	*	10.	7.7
82.9	31.8	~				26	0.0			2.48	0.35		55.80	8	30	133	944	097
B3-1	32.56					1 99		34.36		0.39	0.46		59.21	₹	1	146	717	17.
82-15	24.1					63.6	0.0			2.54	0.78		63.94	17	17	77	927	1 7 5
B3-1A	32.27					60.32		33.92		50	10.1		59.19	3	2	149	254	2,7
B3-19	24.91					67.58		26.61		0.32	0.26		67.39	7	21	163	228	87
1-28	76.6					60.3	0.7	28.69		2.50	0.30		60.71	\$	20	92	157	2 00
B3-18	23.7							25.16		0.23	0.25		68.80	99	17	145	228	5.08
1-1ZH	24.3				67		0.5	25.88		1.60	0.23	1.42		7.7	13	89	125	5 43
B3-3	36.07					55.99		37.77		0.70	0.33			7.7	18	185	217	5.4.5
BZ-560F	<b>:</b>				0.1	61.7	0.5	12.76	_	7.64	0.92	0.08		·				5.60
286	35.03					58.65		36.77			0.08		57.46	3	19	182	255	5 62
BZ-560E	11.9		••		0.1	9.19	0.4	13.31		7.69	0.62	90.0						5.70
BZ-60	₩.					63.1	0.4	9.12	_	9.32	0.0			9	~	21	30	8
B3-4A	25.81					65.5		27.18		0.12	1.19		64.37	52	16	82	150	\$ 88
BZ-110E	16.9				0.1	68.4	0.4	18.09		2.83	1.00	0.08						5.85
BZ-560C	11.7				0.1	62.7	6.0	12.98		7.88	0.0	0.08						6.11
BZ-560	11.7				0.1	67.9	0.5	13.01	_	7.5	0.0	0.08		7	S	18	27	6.22
999	34.65					57.74		36.13			99.0			00	23	152	244	6.35
82.St	10.5					61.4	9.0	11.71	_	8.93	90.0		63.93	10	7	17	ਲ	6.37
BZ-560A	11.7				0.1	62.5	0.8	13.05	_	19.7	9.0	0.08						6.45
BZ-560B	77				0.1	62.3	1.5	13.37	_	7.66		0.08						6.45
BZ-59	174					59.3	0.7	13.83	<u> </u>	88.88	0.12		61.64	90	1	23	38	6.51
717	35.39			_		57.54		37.04			0.03			24	77	160	206	99.9
BT-1	26.2		0.7	0.4	2.8	64.3	0.7	27.50	7.16	0.05	0.23	7.06	63.00	58	17	117	192	6.88
BT-3	22.3	6.6			9.0	64.1	0.3	23.74		0.15	0.23	4.93		43	61	116	180	6.88
BT-2	23.7	6.4	0.7		8.4	6.79	0.3	25.02		0.02	0.23	3.56		48	18	111	175	6.92
BZ-S6	0.	9.8	15.7			63.7	0.5	11.47	_	7.88	90.0			90	7	15	30	7.09
BZ-10	12.4	6.6	5.8		-	61.5	0.5	13.64		7.91	0.12		63.17	7	7	27	7	7.12

Table 3 .... (sheet 3)

		•							-				-				•	
Comp.	O <sup>R</sup> O	OgM	Zr 12	Al2O3 TiO2	ii02	SiO2	Others	CaO	MgO 2	ZrO2 /	Al2O3 T	TiO2	SiO2	CaO	MgO	Sicoz Te	Total	Excess
8Z-55	14.6	1	15.5	0.2		25	0.5	16.14	15.07	7.80	0.12		60.87	Ξ	1	15	2	7
BZ-22	17.1		152			56.7	0.7	18.83	15.02	7.62	0.24		58.29	13	0	27	6	7
97-7	15.2		153		-	58.5	9.0	16.77	15.19	7.68	0.12		60.24	∞	~	2.7	35	7.39
2-28	161	6.6	15.1			54.5	0.0	21.30	15.12	7.55	0.18		55.85	13	7	25	£	7.40
7.74	22.2		15			51.2	8.0	21.16	15.18	7.52	0.18		52.66	17	7	31	15	7.1
3-11	24.91		19.0	_	-	65.11		26.50	8.20	0.30	0.34		99.49	19	27	158	252	7.57
22	X.X.		0.17	_		59.82		35 08	7.73	80.0	0.07		57.04	19	23	170	230	7.5
22	31.08	5.25		0.05		61.33		32.49	7.64		0.03		59.85	8	23	185	289	7.6
21	27.26			0.06		80.59		28.56	177		0.03		63.64	89	20	153	241	7.7
23	29 79		_			62.61		31.10	7.90				0.19	62	11	Ξ	220	7.9
12-57	16.1		13.2	9.3		60.3	9.0	17.19	14.66	6.53	0.18		1179	==	7	15	33	7.9
85-78	12.5		13.6			63.5		13.58	15.12	6.73	0.18		£.19	œ	7	25	ş	8.21
13-20	32.7			16.0		57.57		34.28	8.85		0.52		56.34	95	9	181	250	8.33
<u> </u>	33.1	6.02	0.17	_		58.39		34.4	8.71	0.08	0.15		\$6.65	99	27	133	226	∞
65-28	14.5		13.3			61.2	0.5	15.82	15.18	9.9	0.08		62.33	16	7	6	7	8.52
96	30.91	6.15	0.24			58.81		32.68	9.05	0.12	0.12		58.04	87	37	163	248	80
75:132	30	∞	5.5	5 0.2		65.1		21.16	11.78	2.65	0.12		64.30	31	91	84	28	9.01
19-28	13.2		=	1.0		65.6		14.20	14.51	\$.38	9.0		65.85	9	7	27	7	9.07
21-21	21.3	0.7	10.2			57.8		22.77	14.42	7.96	0.18		57.67	22	13	34	69	9.29
8-Z8	7:		10.8			8.79	0.5	12.19	14.73	5.16	0.12		67.70	01	9	30	20	9.36
33-27	20.98		0.79			68.56		21.97	10.20	0.38	0.45		67.01	3	70	122	196	9.3
9-28	17.2		10.3	3 0.2		8.19	0.5	18.43	14.61	5.02	0.12		61.82	7	10	27	31	0.47
19-28	15.4		10.7			67.9		16.59	14.84	5.25	90.0		63.26	Ξ	10	30	51	9.5
01:17-Z	21		5.6	~		63.5		22.25	12.24	2.70			62.81	25	12	9,	83	9.5
£1-21	27.1		2	0.4		51.2	0.7	29.00	14.74	4.87	0.24		51.15	15	32	28	132	9.63
33-28	18.74	•	0.75			70.81		19.68	10.27	0.36	0.27		69.42	9	3	801	188	6
<u>8</u>	27.14	Ü	9.49			65.23		27.72	9.87	0.23			62.18	7	20	107	171	6
BZ~438	8.±	8.5	2.6	0.1		69.4	0.3	15.74	12.58	2.71	90.0		68.91	11	13	ŝ	9	5
801-28	184		9.9			3		19.44	13.37	3.17	0.12		8.3	2	2	25	<b>\$</b>	<u>ē</u>
0£r-28	17					63.2		18.19	11.41	4.14	0.12		63.12	71	13	29	63	70
107-28	16.1	9.8	8.6	6 0.2		639	_	17.24	14.60	4.19	0.12		63.86	17	=	33	19	<u></u>
82-63	13.1					67.4	_	_	14.56	4.18	90.0		67.20	=	10	37	<b>3</b> 3	9
<i>12</i> 7-28	19.6		80	1 0.2	_	8.09	9.0	_	14.41	3.94	0.12		90.00	29	91	£	88	9
6Z+-Z8	17.8		80	1 0.2	-	62.4	1.1	19.07	14.46	3.95	0.12		62.40	17	12	50	58	9
87-78	18.9		~	8 0.3		61.3	7	20.20	14.57	3.89	0.18		61.16	•	7	2	26	10.50
82-44	14.8	9.6	••	7 0.3		67.3	0.4	15.69	14.16	3.38	0.17			61	2	39	71	<u>ĕ</u>
BZ-610	13.1	_	10.2		0.1	65.2	0.5	14.00	15.76	8.	0.18	0.08		7	2	37	7	<u>ē</u>
BZ-413	18.5		7.	4 0.2		£ 7.	0.7	19.36	14.27	3.53	0.12		62.72	25	=	\$	<b>Z</b>	<u> </u>
BZ-13	61	9.7	7.1	1 0.3		83	0.4	20.06	14.25	3.41	0.17		62.10	32	20	55	107	10.0
	1																	

Table 3 .... (sheet 4)

	Excess	. L.	10.83		10.94	10.99	11.0	1.0	11.11		11.20	11.2	11.2	11.3	7				11.5	11.6		Ξ.		11.6		٠.	11.9		11.9										12.5	_
	Total	7	297	79	77	80	78	72	50	6//	112	9	129	102	112	113			8	06/	_	110	245		171				86		135	130	%	80	98	226	189	101	8	
	SiO2	39	981	12	86	15	45	38	1	19	9	27	8	Z	S	61	115	S	24	88	54	3	142	78	3	67	8	36	25	39	7.1	77	7	\$	15	122	97		\$	
Columbia	MgO	F	35	13	2	91	13	13	13	20	70	=	22	70	22	11	7.7	19	19	7	61	19	30	22	33	20	35	6/	12	16	76	25	25	12	17	11	9	77	6/	
	CaO	7	92	7.7	77	22	20	71	17	38	32	=	35	28	30	30	51	97	25	59	82	31	73	7	*	35	7	28	76	22	38	33	30	53	28	57	52	28	22	
	SiO2	63.58	59.88	29.09	65.03	62.50	£.1	65.33	68.89	61.32	5.53	62.01	60.52	£ 12	63.23	65.21	62.40	63.11	62.53	61.10	63.04	Ĩ.	55.89	61.78	61.13	20.99	54.58	63.89	66.24	65.SE	63.14	<b>3</b> .	8.8	67.16	64.59	60.36	62.24	8.3	65.98	
	Ti02 S							_										0.07											0.07										1.98	
900	AI203 1	0.12	90.0	0.12	0.29	0.12	0.1	0.06	0.29	0.12	0.12	9.0	0.20	0.17	0.17	0.12		0.17	0.57	0.17	0.11	0.11		0.17	0.23	900	0.23	0.11	Q.11	0.1	0.11	0.11	0.11	0.11	0.11	0.23	0.17	0.11	90.0	
1		3.53		3.41	3.34	3.12	3.23	3.15	2.72	3.06	7.7	5.33	2.48	1.57	2.47	2.58		2.42	2.03	2.42	2.47	2.76		2.57	2.39	2.57	2.38	1.93	2.22	2.19	1.70	<u></u>	1.61	1.70	1.93	1.41	1.51	1.65	2.52	
ompositi	MgO ZrO2	<del>1</del>	10.88	14.39	7.58	14.23	14.38	14.28	14.13	14.31	13.76	16.60	13.99	7.	7.08	14.16	<del>8</del> 7.	7.08	14.12	14.21	14.23	1.53	11.67	14.42	14.31	17.82	14.53	13.97	14.31	14.39	14.12	14.02	7.5	14.13	17.41	14.11	14.16	14.27	15.13	
	2 O <sub>2</sub> O	18.34	29.18	21.12	16.76	20.03	18.16	17.18	16.97	21.20	19.05	15.98	22.73	19.03	20.07	17.91	26.11	20.14	20.81	22.10	20.15	18.17	32.45	21.05	21.94	16.82	28.29	20.09	2.	17.76	20.93	19.71	17.69	16.90	18.96	23.90	21.92	19.07	14.33	
	Others (	3		7.0	T.	0.7	0	<del>.</del>	0.5	0.3	7.0	0.5	0.5	0.5	7.0	<b>7</b>		0.	0.5	9.0	0.4	0.4		0.5	9.0	0.4	9.0	7.0	0.3	2	0.4	7	0.3	0.3	0.4	9.0	0.5	0.3	0.3	
	SiO2 (	65	61.83	9.19	96.5	63.5	65.8	8.99	67.4	62.6	65.8	62.4	67.9	65.7	64.9	9.99	65.77	64.8	64.7	62.8	64.7	1.99	59.05	63.2	62.4	67.7	26	7.99	68.3	67.2	65.3	6.9	68.5	69.4	8.99	62.5	64.2	67.1	9.79	
	302								-									<u>.</u>				•							-										2.7	
1100	AIZO3 TiO2	0.2	-C	0.2	S 6	7. 6	0.7	-	0.5	0.2	0.7	0.1	0.5	0.3	0.3	0.7		0.3	0.0	0.3	0.2	0.2		0.3	0.4	 	t:0	0.2	0.7	0.7	0.5	0.5	0.7	0.7	0.2	7.0	0.3	0.7	0.7	
	<u>ي</u>	7.		7.7		2.5	<b>9</b> 0 ,	9.9	5.7	7.0		=	5.2	7.5	5.7	7.5		 -:	4.3	5.1	5.2	30.		<del>``</del>	~	4	~	1.4		9.	3.6	3.5	7.6	3.6	77	~	3.2	3.5	5.3	•
oniposifi	MgO Zr	9.9	7.54	o .	2 ;	> 6	2.0	20 1	7.6	% %	7.6	1.2	9.6	7.6	9.7	9.1	8.12	9.1	8.6	8.6	8.6	9	8.27	6.6	80	2	0	7.	6,6	6.6	90.	œ. œ.	2.7	œ.	10	8.0	8.6	6.6	10.4	
	CaO	17.5	28.13	20.3	9 9	2 ;	7.	7 (	16.2	20.2	8.	2	21.7	18.2	19.7	17.1	25.69	19.3	70.7	21.2	19.3	17.4	32	20.7	20.0	16.1	27.1	16.1	16.4	11	20.2	1.61	<u>.</u>	16.3	18.3	23.1	71.1	18.4	13.7	
	Сошр.	BZ-414	25	111-29	27 70	/01-75			7.78	905-28	207-78	BZ-1	7-79	BZ-101	91-78	8Z-100	419	82-160	177-26	9Z-39	911-78	82 <del>-1</del> 63	714	S0t-28	01-28	75.46	01-28	211-28	92~420	82-119	221-28	82-73	BZ-428	BZ-416	87-718	11-78	25-37	BZ-421	DIZ	

ÇaM	Excess	12.70	12.90	12.98	12.99	13.05	13.17	13.28	13.40	3.44	13.49	13.57	13.64	13.69	13.74	13.96	1.3	14.09	14.27	11.59	11.66	14.71	14.87	15.03	15.04	15.25	15.39	15.57	15.64	15.91	16.15	16.25	16.43	16.49	16.58	16.61	16.71	16.79	16.91	17.26	
	Total	1-	293	214	176	132	254		89	213:	28	127	279	75		191	82	232	87	82	06	5	105	16	83	68	103	•		707	156	227	115	100	119	300	178	=	188	328	
	SiO2 1		17.1	133	101	8	149		37,00	113	45	89	185	45		55	7	137	7	20	20	SS	67	20	47	47	59			112	78	127	99	19	69	178	96	8	105	195	
Solubility	MgO		S	33	31	32	7		14.00	55	28	30	57	13		20	81	0+	61	20	77	77	27	20	<u>∞</u>	21	22			77	7	43	77	24	25	63	39	31	87	99	
	CaC		62	9	7	9	F9		17.00	45	22	29	37	15		79	18	55	74	22	61	77	53	11	81	21	22			tt	37	57	25	24	25	59	43	33	35	63	
	SiO2	65.99	63.96	57.40	61.99	62.25	54.74	63.40	53.54	71.32	64.44	63.34	59.36	65.79	62.63	63.85	63.42	61.76	64.25	62.55	62.86	63.79	63.53	61.17	63.21	63.47	61.50	62.31	62.33	63.28	65.10	57.59	63.07	62.47	63.45	58.89		63.27	68.88	59.59	
	TiO2	0.07						0.07	0.02		1.97			0.74	0.07		0.73	0.07	1.46	7.96				1.32	0.07		0.73	0.07	0.07	0.07	0.65						0.07				
0 % 101	NIZO3	190	0.30	0.27	0.32	0.12	0.35	0.12	90.0	0.11	90.0	0.35	0.33	0.00	0.00	0.11	0.1	0.17	0.06	0.00	0.79	0.0	0.11	0.11	0.57	0.40	0.00	0.00	0.00	0.11	0.06	0.16	0.56	0.78	0.33	0.25	0.11	0.11	90.0	0.82	
ĺ	~	3.40	0.25		10	3.20	_	3.45	3.51	1.06	2.51	1.52		2.72	3.58	2.56	2.76	0.23	2.55	2.31	1.39	2.89	2.45	2.56	1.45	1 46	2.65	2.49	2.51		0.87	0.07	0.28	0.28	0.28	0.11	0.27	0.32	0.58		•
Composition	MgO Z	16.82	13.46	13.25	13.45	16.36	13.52	16.85	16.97	14.61	16.06	16.44	13.97	16.16	17.38	16.63	16.87	14.49	16.87	16.86	17.05	17.66	7.	17.71	17.07	17.11	18.10	18.12	18.31	16.02	17.07	16.48	17.27	17.55	17.19	16.97	17.10	17.22	17.55	18.08	
၁	CaC N	16.08	22.04	29.08	24.10	18.06	31.39	16.11	15.85	12.90	14.97	17.36	26.35	14.24	16.27	16.84	16.10	23.28	14.83	16.26	17.71	15.60	16.47	17.11	17.63	17.57	96.91	16.95	16.82	20.51	16.26	25.70	18.82	18.92	18.74	23.79	21.28	19.08	12.94	21.50	
	Others	7:0			_	<del>7</del> .		0.7	0.5		0.3	0.7		0 3	. 0.8	6.0	0.3	0.2	7.0	0.3	0.7	0.3	0.4	0.3	P. 0	7.0	03	0.7	0.8	0.3	0.7	_	0.3	0.3	0.3		0.3	0.7			
	SiO2 (	64.2	66.17	59.53	61.03	63.5	56.98	64.5	65.3	73.43	£.99	64.9	01.62	67.3	63.9	65.8	9	64.8	799	64.7	55.7	65.7	65.7	62.8	65.7	65.8	63.3	97.9	64.3	67.1	68.7	60.74	66.4	65.8	67.1	61.98	65.6	8.99	72.25	63.66	04 0
	TiO2	0.7						0.7	0.1		7.7			_	0.0		_	0.1	~	2.7	•			7.8	0.1		_	0.1	0.1	0.1	0.9						0.7				
MT.o	VIZO3 T	=	0.52	81.0	0.56	0.2	0.62	0.2	0.1	0.19	0.7	0.6	0.58	0.7	0.7	0.7	0.7	0.3	0.7	0.1	1.7	0.0	0.7	0.2	_	0.7	0.7	0.7	0.1	0.5	0.1	0.28	_	7.	9.0	0.44	0.7	0.7	0.11	61.1	5
	Či	1.7	0.54		0.3	6.7		7.2	7.4	2.23	5.3	5.3		5.7	7.5	ri Vi	90 90	0.5	5.4	67	3.4	6.1	5.2	4.0	<u>~</u>	3.1	26	53	5.3		1.87	91.0	9.0	9.0	9.0	0.23	9.0	0.7	1.24		
ompositie	MgO Zro	11.5	9.34 T.	9.22	9.33	11.2	77.6	11.5	11.7	10:00	11.1	1.3	9.7.3	11.3	11.9	11.5	9.11	10.2	11.7	11.7	11.9	12.2	17.1	12.2	11.9	611	12.5	12.6	12.6	11.4	12	11.66	12.2	12.4	12.2	11.98	12.3	12.2	12.35	12.96	12.76
o	Ca Ca Ca	15.3	21.28	28.15	23.26	17.2	30.5	15.3	15.2	12.4	7.7	16.6	25.53	13.6	. 15:5	16.2	15.4	22.8	Ξ.	15.7	17.2	5	15.9	16.4	17.1	-	16.3	16.4	16.2	20.3	15.9	25.3	18.5	18.6	18.5	23.37	21.3	18.8	12.67	21.44	
	Comp.	BZ-4150B	83-22	B3-25	B3-23	BZ.38	B3-26	BZ-4150.1	BZ-1150	A2-16	110	BZ-435	B3-24	S C	BZ-4150C	82-433	22	818	50	010	9-1-28	167-28	BZ-440	70	BZA-5	B7.A-4	10	82-110.1	BZ-440C	BI4	23	A2-14	BZA-2	BZA-3	BZA-1	7.57	B13	五	A2-15	A2-9	, ,

EP 0 710 628 A2

(	(	Composi	=	W.(0 a					8	tion	mol9 è				Solubility	_		Muc
Comp.	CaO	OgM	74)7	AI203 Ti02	Ti02	SiO2	Others	ÇaÇ	MgC	ZrO2	A[203 ·	Ti02	SiO2.	CaO	MgO	SiO2	Total	Excess
80	16.9				Į.	1 66.2		17.71	18.59	0.83	0.22	0.71	62.54	15		L		.   .
87	17.		9.0	3 0.3	_	67.8	0.7	17.91	18.24	0.36	0.17		63.33	3		3 :	267	
759	17.45	5 12.6				68.33		17.67					25					17.71
5	<u>≈</u>		1.7		~	1 65.1	0.3	18.57		0.78	0	0.70	5 5				261	
12-18	26.23	_		0.66	<b>Y</b> C	56.96		26.85	_	<u>.</u>	0 37	2				3 3		_
312	7.				2 0.1		5 0.2			0 0		0.07						
A2-11	24.28			8 0.25		60.32				6 6	77.0	70.0	_	3 5	£ .		161	
7.7	19.7				_	61.32		19.99			-		47.83					
37.4	18.		•	_			9.0				7.70	0 07			_		150	
37D	18.				2 0.1				_			0.07						18.81
7.5	18.7.		0.14	_	<u>oc</u>	65.69		18.85	_	_	_	5		×	9	5		
3.C	<u> </u>				_	9.99	5 0.7	18.09					62.47				7 7	
<b>%</b>	19.				~	99	0.4	19.05					61.20	Ş				
÷	16.8				2	65.33	_	17.15	20.15				60 63	-		-		
77:77	1.5			8 0.15		70.43		11.78			0.08		98.99		3			19.49
=	 		<b>7</b>	<u> </u>	2 0.1			15.63	1 20.65		0.11	0.07						. `
2	o: ;				~	64.2	0.4	19.71			0.11							_
75.	21.0		0.1		~	59.83		21.58		0.05	0.82		55.80					
75	20.9.							20.79			0.11	-	58.06	_	•	187		20.93
2 5	<u> </u>		= 3		~ ~	. 69.1		7.7		0.03	0.05	0.07	64.22		\$			
2.10	9 5						0.7	16.49		0.13	0.11	0.0	61.48	28				
2.13	7.01				~~~	96.17		16.18			0.27	_	61.62	7	22		2 216	
2-22	936	16 34	280	2 6	·	71.50		14.89	27.31	0.42	90.0		62.32					<b></b>
34	26.6					56.58		74%		0.38	81.0	_	67.14					
61	13.5				100		0 /	13.65		0.02	0.03	0.07	20.92	7 5	8 8	•		
2.20	11.5			0.4		<u>ب</u>		11.71		0.42	0 22	À				153	767	
23	24.4					56.18		24.31	_		0.27	_	52.14		<u>.</u>		_	20.77
2-28	2.0.				<u></u>	78.07		2.08			0.08		73.10	×	×	` ×	· >	
ο.	∞. —				~	64.7	0.2	17.72	23.29		0.11		58.84				_	<u>-</u>
77	23.9.			0.74	_	56.82	_	23.56			0.40	_	52.23					
<b>20</b> }						63	0.5	18.30	24.24	0.13	0.11		57.23		39			00 70
97	. 75		0.3		0.7			14.78		0.13	0.03	0.07		35				
7-17	16.5			<u> </u>		63.56		16.37		0.02	0.18		58.67	47				
8 2 2	16.0					63.68		15.89			0.22		58.82	33	52			24.85
2-23	18.5			0.48	<u></u>	60.2		18.37		0.03	0.26		55.53	35				
2-79		2 19.26	0.98			68.65		8.15		0.45	0.16		64.34	31		183	3.1	
7-32	, O.			0.23		73.09		6.23		0.16	0.12		66.79	×	×	×	×	
A2-27	6.7					71.14		6.70		0.45	0.13		69.59					
	74.0	- }		0.7	<u>.1</u>	54.68		23.44	26.67		0.11		49.77		62	/33		
												1						

Table 3 .... (sheet 7)

		Composi	tion	1,1%					Composit	Ī	nol <sup>9</sup> .6				Solubility			Q.X
Comp.	CaO	MgO	2007	AI2O3 T	TiO2	SiO2 (	Others	CaO	MgO 2r02	-	Alzo3 Ti	TiO2	SiO2	CaO	MgO	SiO2 T	Total	Excess
42-19	18.48			0.54		58.71		18.29	1	ł	ł		54.24			1	- 1	•
12-21	13.74					6F.16		13.51					28.90					
12-31	8.45					67.62		8.26					61.73					
A2-29	4.46			_		71.24		4.34					61.77					
A2-33	197					70.04		4.50			•		63.86					
42-24	13.62	22.74	0.08	0.37		61.38		13.25	30.79	0.04	0.17		55.76		27 87	136	250	30.59
.42-25	10.99					62.36		10.66					\$6.48					
.42-35	8.88					64.12		8.56					57.71					
42-34	6.63					64.85		6.37					58.15					
765	3.9		_	2.12		57.78		3.62					50.03					

## Claims

1. Use as a refractory fibre at temperatures of 1000°C or more for a period of 24 hours of an inorganic fibre for which

a vacuum cast preform of the fibre has a shrinkage of 3.5% or less when exposed to 1260°C for 24 hours and comprising CaO, SiO<sub>2</sub>, MgO, optionally ZrO<sub>2</sub>, optionally less than 0.75mol% Al<sub>2</sub>O<sub>3</sub>, any incidental impurities amounting to less than 2mol% in total, and in which

- a) the SiO<sub>2</sub> excess (defined as the amount of SiO<sub>2</sub> calculated as remaining after the above named constituents are crystallised as silicates) exceeds 21.8mol%;
- b) the amount of CaO is greater than the sum of the amount of MgO and twice the amount of ZrO2; and,
- c) the calculated ratio of diopside to wollastonite does not lie in the range from more than that of fibre E32 to 5.25

 Use of a refractory fibre as claimed in claim 1 in which the incidental impurities include TiO<sub>2</sub> in an amount less than 1.25mol%, preferably less than 0.8mol%.

- 3. Use of a refractory fibre as claimed in claim 1 or claim 2 in which the incidental impurities include Na<sub>2</sub>O in an amount less than 1.0wti%, preferably less than 0.5wt%, more preferably less than 0.3wt%.
- Use of a refractory fibre as claimed in any of claims 1 to 3 in which the incidental impurities include Fe<sub>2</sub>O<sub>3</sub> in an amount less than 1.0wt%, preferably less than 0.6wt%.
- 20 5. Use of a refractory fibre as claimed in any of claims 1 to 4 in which Al<sub>2</sub>O<sub>3</sub> is present in an amount less than 0.5mol%
  - 6. Use of a refractory fibre as claimed in any preceding claim and in which the fibre comprises approximately (in mol%):-

CaO 17.69-20.18 MgO 7.75-17.22 ZrO<sub>2</sub> 0.32-6.19 SiO<sub>2</sub> 63.11-66.54

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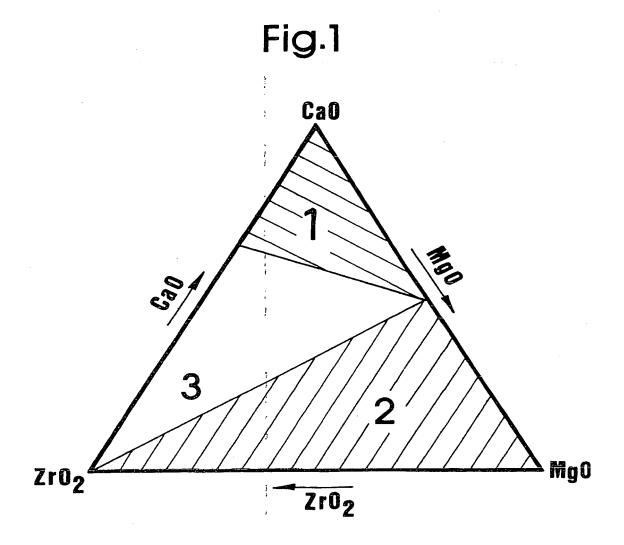
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30 7. Use of a refractory fibre as claimed in claim 6 and in which the fibre comprises approximately (in mol%):-

CaO 32.59-37,18 MgO 0.88-2.92 SiO<sub>2</sub> 61.6-65.52

- 8. Use as a refractory fibre as claimed in any of claims 1 to 7 and which is saline soluble.
- Use as a saline soluble refractory fibre as claimed in claim 8 in which the excess MgO (defined as the amount of MgO less the sum of the amounts of ZrO<sub>2</sub> plus Al<sub>2</sub>O<sub>3</sub>) exceeds 10mol%.
- 10. Use as a saline soluble refractory fibre as claimed in claim 9 in which the excess MgO exceeds 11.3mol%
- 11. Use as a saline soluble refractory fibre as claimed in claim 10 in which the excess MgO exceeds 15.25mol%



(11) EP 0 710 628 A3

(12)

## **EUROPEAN PATENT APPLICATION**

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## (54) Saline soluble inorganic fibres

- (57) Use is disclosed, at temperatures of 1000°C or more for a period of 24 hours, of an inorganic fibre for which a vacuum cast preform of the fibre has a shrinkage of 3.5% or less when exposed to 1260°C for 24 hours and comprising CaO, SiO<sub>2</sub>, MgO, optionally ZrO<sub>2</sub>, optionally less than 0.75mol% Al<sub>2</sub>O<sub>3</sub>, any incidental impurities amounting to less than 2mol% in total, and in which
  - a) the  ${\rm SiO_2}$  excess (defined as the amount of  ${\rm SiO_2}$  calculated as remaining after the above named constituents are crystallised as silicates) exceeds 21.8mol%;
  - b) the amount of CaO is greater than the sum of the amount of MgO and twice the amount of ZrO<sub>2</sub>; and,
  - c) the calculated ratio of diopside to wollastonite does not lie in the range from more than that of fibre E32 to 5.25.

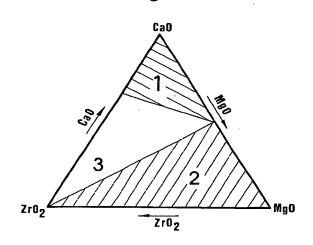


Fig.1

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# EUROPEAN SEARCH REPORT

Application Number EP 95 12 0642

		IDERED TO BE RELEVAN		<del></del>
Category	Citation of document with of relevant p	indication, where appropriate, passages	Relevant to claim	CLASSIFICATION OF TH APPLICATION (Int.Cl.5)
P,L, X	WO-A-93 15028 (THE PLC) * the whole docume	MORGAN CRUCIBLE COMPANY	1-11	C03C13/00
x,c	WO-A-87 05007 (MAN * claims 1-5 *	VILLE CORPORATION)	1-11	
х, с	WO-A-89 12032 (MAN' * claim 1 *	VILLE SALES CORPORATION)	1-6,8-11	
	WO-A-92 09536 (PAR * claim 1 *	DC OY AB)	1-5,8-11	
		·	ŀ	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
		·	ſ	C03C
•				
<u> </u>	The present search report has be	PRI drawn un for all claims		
	Place of search	Date of completion of the search	_,	
_	HE HAGUE	3 April 1996	Reed	ijk, A
X : partici Y : partici	TEGORY OF CITED DOCUMEN plarly relevant if taken alone plarly relevant if combined with anotent on of the same category	T: theory or principle E: earlier patent docum	underlying the in ment, but publish he application	

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